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APPROXIMATE SELF-CONSISTENT FIELD CALCULATIONS OF MOLECULAR POTENTIAL SURFACES

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APPROXIMATE
SELF-CONSISTENT FIELD CALCULATIONS
OF MOLECULAR POTENTIAL SURFACES

by

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ABSTRACT

The Approximate Self-Consistent Field Molecular Orbital Theory (ASCFT) with complete neglect of differential overlap (CNDO) has been applied to the calculation of electronic structure for several selected molecules in this text. The theory leads to calculated equilibrium geometry configurations and the barrier to internal rotation of ethane, inversion barrier of ammonia and the barrier for cis to trans conversion for difluorodiazine. These results are in reasonable agreement with experimental values in most cases. The stretching force constants are higher than experimental values by a factor of approximately two. The orbital energy levels for ammonia and for oxygen difluoride as a function of bond angles were in reasonable agreement with the full LCAO-SCF Calculations. A variation of parameters to find a new set of parameters was attempted with unsuccessful results.

The Extended Hückel Theory (EHT) can be applied to aliphatic hydrocarbons but its application to non-hydrocarbon molecules is quite limited.

TABLE OF CONTENTS

Section	Page
I Introduction	9
II Hückel molecular orbital theory	9
III Extended Hückel theory	15
IV Approximate self-consistent field Molecular orbital theory	17
1. SCF equation	19
2. Theory with complete neglect of differential overlap (CNDO)	21
3. Choice of Parameters of CNDO1 and CNDO2.	26
V Discussion of Results	28
1. Comparison of the equilibrium configurations and force constants.	29
2. Water molecule (H_2O).	30
3. Ammonia molecule (NH_3).	30
4. Ethane molecule (C_2H_6).	35
5. Methane and Methylfluoride (CH_4 and CH_3F).	38
6. Difluorodiazine (N_2F_2).	39
7. Oxygen difluoride.	43
8. Hydrogen Peroxide.	45
9. Homonuclear diatomic molecules	46
VI Conclusions	48
Bibliography	50
Appendix	
I Computer program for ASCFT.	53
II Computer output of H_2O (Sample).	94

LIST OF TABLES

1. Slater exponents for valence Shell S and P atomic orbitals.
2. Bonding parameters β_A^0 (in e.v.).
3. "Average" ionization potentials I_μ (e.v.).
4. Difference between CND01 and CND02.
5. Matrix elements from atomic data. $U_{\mu\mu}$ (CND02).
6. Comparison of equilibrium geometry and force constants.
7. Calculation of R_{OH} and $\angle HOH$ for H_2O .
8. Comparison of the results of calculations for NH_3 .
9. Change in barrier for NH_3 w.r.t. minimizing parameters.
10. Comparison of Ethane between EHT and ASCFT calculation.
11. Comparison of barrier for Ethane.
12. Comparison of r , θ , k_r and k_θ between CH_4 and CH_3F .
13. Results of experiments and calculations for N_2F_2 .
14. Equilibrium configuration between cis and trans for N_2F_2 molecule.
15. Comparison of barrier between $C_{2v}(C_2h)$ and $C_2(C_{2v})$ for N_2F_2 .
16. Equilibrium configurations and some partial derivatives for homonuclear diatomic molecules.

1. The first part of the paper is devoted to the study of the	1
2. properties of the solutions of the problem	2
3. 4. The second part of the paper is devoted to the study of the	3
4. properties of the solutions of the problem	4
5. 5. The third part of the paper is devoted to the study of the	5
6. properties of the solutions of the problem	6
7. 6. The fourth part of the paper is devoted to the study of the	7
8. properties of the solutions of the problem	8
9. 7. The fifth part of the paper is devoted to the study of the	9
10. properties of the solutions of the problem	10
11. 8. The sixth part of the paper is devoted to the study of the	11
12. properties of the solutions of the problem	12
13. 9. The seventh part of the paper is devoted to the study of the	13
14. properties of the solutions of the problem	14
15. 10. The eighth part of the paper is devoted to the study of the	15
16. properties of the solutions of the problem	16
17. 11. The ninth part of the paper is devoted to the study of the	17
18. properties of the solutions of the problem	18
19. 12. The tenth part of the paper is devoted to the study of the	19
20. properties of the solutions of the problem	20
21. 13. The eleventh part of the paper is devoted to the study of the	21
22. properties of the solutions of the problem	22
23. 14. The twelfth part of the paper is devoted to the study of the	23
24. properties of the solutions of the problem	24
25. 15. The thirteenth part of the paper is devoted to the study of the	25
26. properties of the solutions of the problem	26
27. 16. The fourteenth part of the paper is devoted to the study of the	27
28. properties of the solutions of the problem	28
29. 17. The fifteenth part of the paper is devoted to the study of the	29
30. properties of the solutions of the problem	30
31. 18. The sixteenth part of the paper is devoted to the study of the	31
32. properties of the solutions of the problem	32
33. 19. The seventeenth part of the paper is devoted to the study of the	33
34. properties of the solutions of the problem	34
35. 20. The eighteenth part of the paper is devoted to the study of the	35
36. properties of the solutions of the problem	36
37. 21. The nineteenth part of the paper is devoted to the study of the	37
38. properties of the solutions of the problem	38
39. 22. The twentieth part of the paper is devoted to the study of the	39
40. properties of the solutions of the problem	40
41. 23. The twenty-first part of the paper is devoted to the study of the	41
42. properties of the solutions of the problem	42
43. 24. The twenty-second part of the paper is devoted to the study of the	43
44. properties of the solutions of the problem	44
45. 25. The twenty-third part of the paper is devoted to the study of the	45
46. properties of the solutions of the problem	46
47. 26. The twenty-fourth part of the paper is devoted to the study of the	47
48. properties of the solutions of the problem	48
49. 27. The twenty-fifth part of the paper is devoted to the study of the	49
50. properties of the solutions of the problem	50
51. 28. The twenty-sixth part of the paper is devoted to the study of the	51
52. properties of the solutions of the problem	52
53. 29. The twenty-seventh part of the paper is devoted to the study of the	53
54. properties of the solutions of the problem	54
55. 30. The twenty-eighth part of the paper is devoted to the study of the	55
56. properties of the solutions of the problem	56
57. 31. The twenty-ninth part of the paper is devoted to the study of the	57
58. properties of the solutions of the problem	58
59. 32. The thirtieth part of the paper is devoted to the study of the	59
60. properties of the solutions of the problem	60
61. 33. The thirty-first part of the paper is devoted to the study of the	61
62. properties of the solutions of the problem	62
63. 34. The thirty-second part of the paper is devoted to the study of the	63
64. properties of the solutions of the problem	64
65. 35. The thirty-third part of the paper is devoted to the study of the	65
66. properties of the solutions of the problem	66
67. 36. The thirty-fourth part of the paper is devoted to the study of the	67
68. properties of the solutions of the problem	68
69. 37. The thirty-fifth part of the paper is devoted to the study of the	69
70. properties of the solutions of the problem	70
71. 38. The thirty-sixth part of the paper is devoted to the study of the	71
72. properties of the solutions of the problem	72
73. 39. The thirty-seventh part of the paper is devoted to the study of the	73
74. properties of the solutions of the problem	74
75. 40. The thirty-eighth part of the paper is devoted to the study of the	75
76. properties of the solutions of the problem	76
77. 41. The thirty-ninth part of the paper is devoted to the study of the	77
78. properties of the solutions of the problem	78
79. 42. The fortieth part of the paper is devoted to the study of the	79
80. properties of the solutions of the problem	80
81. 43. The forty-first part of the paper is devoted to the study of the	81
82. properties of the solutions of the problem	82
83. 44. The forty-second part of the paper is devoted to the study of the	83
84. properties of the solutions of the problem	84
85. 45. The forty-third part of the paper is devoted to the study of the	85
86. properties of the solutions of the problem	86
87. 46. The forty-fourth part of the paper is devoted to the study of the	87
88. properties of the solutions of the problem	88
89. 47. The forty-fifth part of the paper is devoted to the study of the	89
90. properties of the solutions of the problem	90
91. 48. The forty-sixth part of the paper is devoted to the study of the	91
92. properties of the solutions of the problem	92
93. 49. The forty-seventh part of the paper is devoted to the study of the	93
94. properties of the solutions of the problem	94
95. 50. The forty-eighth part of the paper is devoted to the study of the	95
96. properties of the solutions of the problem	96
97. 51. The forty-ninth part of the paper is devoted to the study of the	97
98. properties of the solutions of the problem	98
99. 52. The fiftieth part of the paper is devoted to the study of the	99
100. properties of the solutions of the problem	100

LIST OF ILLUSTRATIONS

1. Orbital Energy of NH_3 as a function of the pyramid height (ASCFT and full LCAOSCFT).
2. Orbital energy of NH_3 as a function of the Pyramid height (EHT).
3. Barrier for N_2F_2 as a function of $\angle \text{NNF}$
4. Orbital energy of F_2O as a function of $\angle \text{FOF}$. (ASCFT and full LCAOSCFT).
5. Structural parameters of H_2O_2 .

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I. INTRODUCTION

There are many levels of sophistication for the calculation of electronic structure using molecular orbital methods. The simplest approach is the Hückel Molecular Orbital Theory (HMO). This is one of the semiempirical methods which is used extensively in the quantum mechanical study of the mobile electrons of conjugated molecules. The HMO was extended by many people. One of the theories examined in this paper is the "Extended Hückel Theory (EHT)" which was developed by Roald Hoffmann (1). A higher level of sophistication is the self-consistent field (SCF) molecular orbital calculation. One of those methods which has recently been developed is based on a theory introduced by J. A. Pople: "Approximate Self-Consistent Field Molecular Orbital Theory (ASCFT)" (2), (3), (4). This ASCFT Calculation is predominantly used throughout this text.

We can say molecular orbital methods are "curve fitting". They are really based on semiempirical methods. The purposes of the calculation described herein are the prediction of potential surface by Pople's theory to examine and to try to improve the agreement of a calculated potential surface with an experimental potential surface.

The background describing each of these theories will be discussed in the next section.

II. Hückel Molecular Orbital Theory (HMO)

In this theory, the mobile electrons can be treated as occupying a set of delocalized molecular orbitals (by the Pauli Exclusion Principle, not more than two electrons in each molecular orbital). These molecular

orbitals are eigenfunctions of a one electron Hamiltonian. The orbitals are approximated by a linear combination of atomic orbitals (LCAO) centered on various atoms. The Slater type atomic orbitals (5) are generally used as approximations to the actual atomic orbitals for each atom. When this theory is applied to a wide range of molecules, it has the advantage of great simplicity but serious discrepancies result because of the neglect of interelectronic repulsions for the case of many electrons.

For the unsaturated molecules: The π - molecular orbitals are formed by a LCAO of the $2p_z$ atomic orbitals which, it is assumed, share the same nodal plane. In $N-\pi$ electron systems, the molecular orbitals are given by

$$\Psi_j = \sum_{z=1}^N C_{jz} \Phi_z \quad (j=1, \dots, N) \quad (1.1)$$

where Ψ_j represents the j^{th} molecular orbital, Φ_z represents the atomic orbital in the z^{th} atom and C_{jz} represents the coefficients of the j^{th} molecular orbital and the z^{th} atom (atomic orbital). It is noted that the subscript i, j, k, l etc. stand for the molecular orbitals and $\mu, \nu, \sigma, \lambda$ etc. stand for the atoms or atomic orbitals.

From a given electron Hamiltonian, Equation (1.1) must satisfy the equation

$$\mathcal{H}\Psi_j = E_j\Psi_j \quad (1.2)$$

Where E_j is the eigenvalue of the j^{th} state, Ψ_j is a column matrix, and \mathcal{H} is the Hamiltonian operator. This can be put in matrix form:

$$(A) \begin{pmatrix} \psi_1 \\ \vdots \\ \psi_N \end{pmatrix} = \begin{pmatrix} E_1 & 0 & \dots & 0 \\ 0 & E_2 & & 0 \\ \vdots & & \ddots & \vdots \\ 0 & \dots & 0 & E_N \end{pmatrix} \begin{pmatrix} \psi_1 \\ \vdots \\ \psi_N \end{pmatrix} \quad (1.2)$$

We multiply equation (1.2) by ψ_i^* and integrate over all space, $d\tau$, then we obtain

$$\int \psi_i^* A \psi_j d\tau = \int \psi_i^* E_j \psi_j d\tau \quad (1.3)$$

Substituting equation (1.1) into (1.3)

$$\sum_{\mu} \sum_{\nu} C_{i\mu}^* C_{j\nu} \int \phi_{\mu}^* A \phi_{\nu} d\tau = \sum_{\mu} \sum_{\nu} C_{i\mu}^* C_{j\nu} E_j \int \phi_{\mu}^* \phi_{\nu} d\tau \quad (1.4)$$

Defining

$$H_{\mu\nu} = \int \phi_{\mu}^* A \phi_{\nu} d\tau \quad (1.5)$$

and

$$S_{\mu\nu} = \int \phi_{\mu}^* \phi_{\nu} d\tau \quad (1.6)$$

We may write equation (1.4)

$$\sum_{\mu, \nu} C_{i\mu} C_{j\nu} H_{\mu\nu} = E_j \sum_{\mu, \nu} C_{i\mu} C_{j\nu} S_{\mu\nu} \quad (1.7)$$

Taking the derivative of equation (1.7) with respect to $C_{k\lambda}$ to minimize the energy ($\partial E_j / \partial C_{k\lambda} = 0$), we obtain

$$\sum_{\mu} C_{k\mu} H_{\mu\lambda} + \sum_{\nu} C_{k\nu} H_{\lambda\nu} = E_k \left(\sum_{\mu} C_{k\mu} S_{\mu\lambda} + \sum_{\nu} C_{k\nu} S_{\lambda\nu} \right) \quad (1.8)$$

It may be shown that

$$S_{\mu\nu} = S_{\nu\mu} \quad (1.9)$$

$$H_{\mu\nu} = H_{\nu\mu} \quad (1.10)$$

Therefore we obtain the equation

$$\sum_{\mu} C_{k\mu} H_{\mu\lambda} = E_k \sum_{\mu} C_{k\mu} S_{\mu\lambda} \quad (1.11)$$

or

$$\sum_{\mu} C_{k\mu} (H_{\mu\lambda} - E_k S_{\mu\lambda}) = 0 \quad (1.12)$$

This equation (1.12) is the well-known secular equation and gives rise to the secular determinant:

$$| H_{\mu\lambda} - E_k S_{\mu\lambda} | = 0 \quad (1.13)$$

Equation (1.13) is the non-trivial solution of (1.12).

Now we discuss the Hermitian Property of the Matrices $(H_{\mu\lambda})$ and $(S_{\mu\lambda})$. A matrix H is said to be Hermitian if it is equal to the conjugate of its transpose, i.e.,

$$\overline{H'} = H$$

Where $H = (H_{\mu\lambda})$ and $\overline{H'} = (\overline{H_{\lambda\mu}})$ (1.14)
 $(\mu, \lambda = 1, 2, \dots, N)$

By definition, a real Hermitian matrix is symmetric, but an imaginary symmetric matrix is not necessarily an Hermitian matrix. It is noted that the eigenvalues of an Hermitian matrix are all real.

Next we discuss some transformation properties. In general, the atomic orbital ϕ_{μ} does not form a complete orthonormal set. This basis, ϕ_{μ} , can be transformed into an orthonormal basis by using a unitary transformation matrix such that

$$\phi_{\mu}^{\text{new}} = \sum_{\lambda} T_{\lambda\mu} \phi_{\lambda}^{\text{old}} \quad (1.15)$$

where ϕ_{μ}^{new} is the new orthonormal basis formed by transforming the old basis $\phi_{\lambda}^{\text{old}}$ in N dimensional space and $T_{\lambda\mu}$ is the transformation matrix element. The old H can also be transformed into a new basis such that

$$H_{\mu\nu}^{\text{new}} = \sum_{\lambda, \sigma} T_{\mu\sigma}^* T_{\nu\lambda} \int \phi_{\sigma}^* \mathcal{H} \phi_{\lambda} d\tau \quad (1.16)$$

It may be recalled that the old basis is $H_{\sigma\lambda}^{\text{old}} = \int \phi_{\sigma}^* \mathcal{H} \phi_{\lambda} d\tau$.

Therefore equation (1.16) can be rewritten

$$H_{\mu\nu}^{\text{new}} = \sum_{\sigma, \lambda} T_{\mu\sigma}^* H_{\sigma\lambda}^{\text{old}} T_{\nu\lambda} \quad (1.16)'$$

or

$$H_{\mu\nu}^{\text{new}} = \sum_{\sigma, \lambda} T_{\mu\sigma}^* H_{\sigma\lambda}^{\text{old}} T_{\lambda\nu}' \quad (1.17)$$

It is noted that if the transformations were made:

$$\phi_z^{\text{new}} = \sum_{\lambda} \phi_{\lambda} T_{\lambda z} \quad (1.18)$$

then the equation (1.17) becomes

$$H_{\mu\nu}^{\text{new}} = \sum_{\sigma, \lambda} T_{\mu\sigma}^{\star'} H_{\sigma\lambda}^{\text{old}} T_{\lambda\nu} \quad (1.19)$$

Equations (1.17) and (1.19) can be written by matrix notation such that

$$H^{\text{new}} = T^{\star} H^{\text{old}} T' \quad (1.17)'$$

and

$$H^{\text{new}} = T^{\star'} H^{\text{old}} T \quad (1.19)'$$

From equation (1.19)', if T is a unitary matrix ($T^{-1} = T^{\star'}$) then we have

$$H^{\text{new}} = T^{-1} H^{\text{old}} T \quad (1.20)$$

This equation (1.20) is frequently used and usually T is real and H^{old} is a symmetric matrix.

Referring to the secular equation (1.12), we define $\lambda_{kk} = E_k$, then

$$\sum_{\mu} (H_{\lambda\mu} C_{\mu k} - S_{\lambda\mu} C_{\mu k} \lambda_{kk}) = 0 \quad (1.21)$$

This can be expressed in matrix notation in the following manner

$$HC - SC\lambda = 0 \quad (1.21)'$$

where

$$\begin{aligned} H &= (H_{\lambda\mu}) & \lambda &= (\lambda_{kk}) \\ C &= (C_{\mu k}) & & \\ S &= (S_{\lambda\mu}) & (\lambda, \mu, k &= 1, \dots, N) \end{aligned}$$

Therefore, we obtain

$$\lambda = (\lambda_{kk}) = C^{-1} (S^{-1} H) C \quad (1.22)$$

It is generally true that the matrix $(S^{-1}H)$ may not be symmetric. In equation (1.22), the eigenvalue cannot be obtained by methods usually employed to diagonalize Hermitian matrices. One way to solve this problem is to transform the matrix S to an orthonormal basis, then diagonalize the H matrix. The procedures are described as follows: Using the transformation matrix Q such that $\psi = Q\phi$, we transform the matrix S to the identity matrix I

$$S^{\text{new}} = I = QS^{\text{old}}Q' \quad (1.23)$$

or

$$S^{\text{old}} = (Q'Q)^{-1} \quad (1.24)$$

Also we diagonalize the matrix S by a unitary transformation matrix T such that

$$\lambda = TS^{\text{old}}T' \quad (1.25)$$

or

$$\begin{aligned} S^{\text{old}} &= (T'\lambda^{-1}T)^{-1} \\ &= [(T'\lambda^{-1/2}T)'(T'\lambda^{-1/2}T)]^{-1} \end{aligned} \quad (1.26)$$

Equating equation (1.24) and (1.26), we obtain

$$Q = T'\lambda^{-1/2}T \quad (1.27)$$

Then we transform the old basis H to the new basis by the transformation matrix Q such that

$$\begin{aligned} H^{\text{new}} &= QH^{\text{old}}Q' \\ &= (T'\lambda^{-1/2}T)(H^{\text{old}})(T'\lambda^{-1/2}T)' \end{aligned} \quad (1.28)$$

Finally we can diagonalize H^{new} by the matrix U . Then we obtain the eigenvalues

$$\begin{aligned} E &= UH^{\text{new}}U' \\ &= (UT'\lambda^{-1/2}T)(H^{\text{old}})(UT'\lambda^{-1/2}T)' \end{aligned} \quad (1.29)$$

where U is the matrix which diagonalizes the H^{new} and T is the unitary matrix which diagonalizes S. Also the correct eigenfunctions are

$$\Psi = UT'\lambda^{-1/2}T\Phi \quad (1.30)$$

The general operations for the application of HMO theory to specific problems are

- (a) Setting up the Secular determinant
- (b) Expanding the Secular determinant
- (c) Finding the eigenvalues
- (d) Determining the M.O.'s by finding the eigenvectors.

III. Extended Hückel Theory (EHT)

Hückel calculations originally were applied exclusively for the Planar conjugated and aromatic systems of π electrons with the neglect of overlap for non-adjacent atoms. In the extended Hückel theory (EHT), Roald Hoffmann (1) expanded the basis set to consist of 2s and 2p orbitals for Carbon atoms and 1s orbitals for Hydrogen, with the inclusion of all overlap integrals. The EHT can calculate molecular orbitals for the aliphatic and aromatic compounds which gives good results for most hydrocarbons because of the reasonable set of parameters chosen for the calculations. The parameters are nicely adjusted to the self-consistent value for the hydrocarbons but when the EHT is applied to non-hydrocarbons, it is not as successful, and even predicts a lack of minima in many bond stretching motions.

III-A. Method of Calculation

For the calculation of the molecule C_nH_m , we use a basis set

consisting of m-Hydrogen Slater orbitals, n-2s and 3n-2P orbitals. The Slater exponents were selected to be 1.0 for Hydrogen and 1.625 for Carbon throughout the calculations. It is noted that 1.20 was selected for Hydrogen in the calculation of the ethane molecule. Those values are listed in Table 1. The order of the matrix is $4n + m$ which gives the number of energy levels of the system and the eigenvalue E's for off diagonal matrix elements are retained in the Secular Equation.

TABLE 1

Slater exponents for valence Shell S and P atomic orbitals.

H	1.0*	C ⁻	1.45	O ⁻	2.10
Li	0.65	C	1.625	O	2.275
Be	0.975	C ⁺	1.80	O ⁺	2.45
B ⁻	1.125	N	1.95	F	2.60
B	1.30	N ⁺	2.125		

* Present calculations we carried out using 1.2 for Hydrogen.

The diagonal elements $H_{\mu\mu}$ are chosen to be valence state ionization potentials; the particular values used are essentially those of Skinner and Pritchard (6). For example, the SP^3 valence state ionization potentials for Carbon and 1s Hydrogen atoms have the following values:

$$\begin{aligned}
 H_{\mu\mu}(C_{2p}) &= -11.4 \text{ e.v.} \\
 H_{\mu\mu}(C_{2s}) &= -21.4 \text{ e.v.} \\
 H_{\mu\mu}(H_{1s}) &= -13.6 \text{ e.v.}
 \end{aligned}
 \tag{2.1}$$

The choice of the off-diagonal term $H_{\mu\nu}$ is approximated as

$$H_{\mu z} = 0.5 K (H_{\mu\mu} + H_{zz}) (S_{\mu z}) \quad (2.2)$$

The approximation (2.2) was first discussed by M \ddot{u} lliken (7) and used in the M.O. Calculations by Wolfsberg and Helmholtz (8).

The value of K in equation (2.2) was chosen to be 1.75. These calculations give fairly good results for hydrocarbons.

IV. Approximate Self-Consistent Field Molecular Orbital Theory (ASCFT)

Approximate methods for obtaining self-consistent field molecular orbitals have recently been developed by J. A. Pople (2), (3), (4). Slater type orbitals (5) are used as basis functions. Overlap integrals between two different atoms were calculated using the formula given by M \ddot{u} lliken, Rieke, Orloff and Orloff (9). It is assumed that the Slater type atomic orbitals are real atomic orbitals, and that the M.O.'s for the ground state are obtained by Linear Combinations of Slater type atomic orbitals. If the Coefficients in the LCAO Molecular orbitals are chosen to minimize the total energy, one obtains LCAO - SCF orbitals. The best LCAO approximation to SCF functions were first given by Roothaan (10). It is noted that the EHT treated all the electrons independently. EHT wave functions are used as a starting point for the self-consistent field iterations in this ASCFT.

The SCF methods were developed using two approximations based on the neglect of the differential overlap between all valence atomic orbitals. One of these involves complete neglect of differential overlap (CNDO) in all basis sets connected by the transformations as mentioned in Section I, that is: the off-diagonal elements of overlap matrix in the Hamiltonian matrix are to be neglected. The other involves the

neglect of the products of $\phi_{\mu}(i)\phi_{\nu}(i)$ of any two atomic orbitals ϕ_{μ} and ϕ_{ν} in all electron-repulsion integrals. This complete neglect of differential overlap of all basis sets will result in non-orthonormal basis sets.

The CNDO method in ASCFT should be regarded as an approximation to a full LCAO - SCF calculation which uses a minimal basis containing only inner-shell and valence-shell atomic orbitals. The Slater exponents used in these calculations are listed in Table 1 (for Hydrogen, 1.2 is used). The values for β° and ionization potentials in 2s and 2p atomic orbitals from Lithium to Fluorine were set semiempirically. Those values used in these calculations are tabulated in Table 2 and Table 3 respectively.

TABLE 2								
Bonding Parameters β_A° (in e.v.)								
Atom	H	Li	Be	B	C	N	O	F
	9	9	13	17	21	25	31	39

TABLE 3								
"Average" Ionization Potentials I_{μ} (in. e.v.)								
Atom	H	Li	Be	B	C	N	O	F
1s	13.06	--	--	--	--	--	--	--
2s	--	5.39	9.32	14.05	19.44	25.58	32.38	40.20
2P	--	3.54	5.96	8.30	10.67	13.19	15.85	18.66

The CNDO method of ASCFT can be used for closed ground shell structures and doublets, but a triplet structure is not available with the computer program used (for example O₂, B₂ and C₂). The computer program is presented in Appendix 1.

IV-1. Self-Consistent Field (SCF) Equation

The initial discussion covers Roothaan's LCAO - SCF method (10) as a basis for calculating the MO's of a molecule, paying particular attention to transformation properties. The 1s Hydrogen and valence shell electrons for Li to F are assigned to LCAO molecular orbitals. Minimization of total energy by a variation principle with SCF orbitals leads to a series of simultaneous non-Linear equations, the so called Hartree Fock equations (11), which are applied to LCAO molecular orbitals with a closed shell configuration. These equations were shown by Roothaan to reduce to the form (10)

$$\sum_{\mu} F_{\mu\nu} C_{\nu i} = \sum_{\mu} S_{\mu\nu} C_{\nu i} \epsilon_i \quad (4.1)$$

where (using atomic units)

$$F_{\mu\nu} = H_{\mu\nu} + G_{\mu\nu} \quad (4.2)$$

$$H_{\mu\nu} = \int \phi_{\mu}^* \left(-\frac{1}{2} \nabla^2 - \sum_A \frac{1}{r_A} \right) \phi_{\nu} d\tau \quad (4.3)$$

$$G_{\mu\nu} = \sum_{\lambda, \sigma} P_{\lambda\sigma} \left[(\mu\nu|\lambda\sigma) - \frac{1}{2} (\mu\sigma|\nu\lambda) \right] \quad (4.4)$$

$$(\mu\nu|\lambda\sigma) = \iint \phi_{\mu}^{*(1)} \phi_{\nu}^{(1)} \frac{1}{r_{12}} \phi_{\lambda}^{*(2)} \phi_{\sigma}^{(2)} d\tau_1 d\tau_2 \quad (4.5)$$

$$S_{\mu\nu} = \int \phi_{\mu}^* \phi_{\nu} d\tau \quad (4.6)$$

$$P_{\lambda\sigma} = 2 \sum_{\lambda}^{\text{occ}} C_{\lambda\lambda}^* C_{\lambda\sigma} \quad (4.7)$$

Where E_i is the orbital energy for the i^{th} M.O. $H_{\mu\nu}$ is the matrix element of the one electron Hamiltonian including the kinetic energy and the Potential energy in the electrostatic field of the core, this being written as a sum of potentials $V_A(r)$ for various atoms A in the molecule. $G_{\mu\nu}$ is the matrix element of the potential due to valence electrons and depends on the M.O.'s via the population matrix $P_{\lambda\sigma}$.

The total energy of the molecule is obtained by adding the repulsion energy between isolated cores and the separated valence electrons. The repulsion term can be approximated by a point charge model

$$E_{\text{total}} = E_{\text{electronic}} + \sum_A \sum_B Z_A Z_B / R_{AB} \quad (4.8)$$

where Z_A is the core charge of atom A. The electronic energy is given by

$$E_{\text{operator}} = 2 \sum_{\lambda} H_{\lambda\lambda} + \sum_{\lambda, j} (2 J_{\lambda j} - K_{\lambda j}) \quad (4.9)$$

$$\begin{aligned} E_{\text{electronic}} &= 2 \sum_{\mu, \nu, \lambda} C_{\mu\lambda} C_{\nu\lambda} H_{\mu\nu} + \sum_{\mu, \nu, \lambda} C_{\mu\lambda} C_{\nu\lambda} G_{\mu\nu} \\ &= \sum_{\mu, \nu} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \sum_{\mu, \nu} P_{\mu\nu} G_{\mu\nu} \end{aligned}$$

$$\begin{aligned}
E_{\text{elect.}} &= \frac{1}{2} \sum_{\mu, \nu} P_{\mu\nu} [2 H_{\mu\nu} + G_{\mu\nu}] \\
&= \frac{1}{2} \sum_{\mu, \nu} P_{\mu\nu} [H_{\mu\nu} + F_{\mu\nu}]
\end{aligned} \tag{4.10}$$

IV-2. Theory with Complete Neglect of Differential Overlap (CNDO)

First consider the simplest version of the theory which involves the complete neglect of differential overlap between atomic orbitals on the same atom. The approximations are given below.

Approximation A

The atomic orbitals ϕ_μ are treated as if they form an orthonormal set such that $S_{\mu\nu} = \delta_{\mu\nu}$ and then the $C_{i\mu}$ forms an orthonormal matrix. The condition for orthonormality becomes:

$$\sum_{\mu} C_{i\mu} C_{j\mu} = \delta_{ij} \tag{4.11}$$

With this approximation, the diagonal matrix elements $P_{\mu\mu}$ (electron density) correspond to the electron populations of the atomic orbitals ϕ_μ and

$$\sum_{\mu} P_{\mu\mu} = 2N \tag{4.12}$$

where $2N$ is the number of valence electrons.

Approximation B.

Equations (4.4) are neglected because of the orthonormality of atomic orbitals. This means $(\mu\nu|\lambda\sigma)$ is zero unless $\mu = \nu$ and $\lambda = \sigma$. The non-zero values will be written $\gamma_{\lambda\mu}$ such that

$$\gamma_{\lambda\mu} = (\lambda\lambda | \mu\mu) \quad (4.13)$$

Approximation C

The electron-interaction integrals $\gamma_{\mu\nu}$ are assumed to depend only on the atoms to which the orbitals ϕ_μ and ϕ_ν belong and not on the actual type of the orbitals. This means that there remains only a set of atomic electron-interaction integrals γ_{AB} measuring an average repulsion between an electron in valence atomic orbital on atom A and another in a valence orbital on atom B. The set of atomic orbitals on one particular atom A is replaced by an alternative set t_m ,

$$t_m = \sum_\mu O_{m\mu} \phi_\mu \quad (4.14)$$

A general electron-repulsion integral in this new basis set is given by

$$(t_m t_n | \phi_\lambda \phi_\lambda) = \sum_{\mu\nu} O_{m\mu} O_{n\nu} (\phi_\mu \phi_\nu | \phi_\lambda \phi_\lambda) \quad (4.15)$$

Now we apply approximation C, then equation (4.15) becomes

$$(t_m t_n | \phi_\lambda \phi_\lambda) = \gamma_{AB} \delta_{mn} \quad (4.16)$$

It is noted that equation (4.16) is invariant under the orthogonal transformation matrix **O** which gives the new basis **t**.

Using approximation A, and B, the matrix elements $F_{\mu\nu}$ become

$$\begin{aligned} F_{\mu\mu} &= H_{\mu\mu} + G_{\mu\mu} \\ &= H_{\mu\mu} + \sum_{\lambda\sigma} P_{\lambda\sigma} [(\mu\mu | \lambda\sigma) - \frac{1}{2}(\mu\sigma | \mu\lambda)] \\ &= H_{\mu\mu} - \frac{1}{2} P_{\mu\mu} \gamma_{\mu\mu} + \sum_{\sigma(\neq\mu)} P_{\sigma\sigma} \gamma_{\mu\sigma} \end{aligned} \quad (4.17)$$

$$F_{\mu\nu} = H_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \delta_{\mu\nu} \quad (4.18)$$

Equation (4.17) and (4.18) can be rewritten by approximation C

$$F_{\mu\mu} = H_{\mu\mu} - \frac{1}{2} P_{\mu\mu} \delta_{AA} + P_{AA} \delta_{AA} + \sum_{(B \neq A)} P_{BB} \delta_{AB} \quad (4.19)$$

$$F_{\mu\nu} = H_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \delta_{AB} \quad (4.20)$$

where μ belongs to atom A and P_{BB} is the total valence electron density on atom B.

$$P_{BB} = \sum_{\nu}^B P_{\nu\nu} \quad (4.21)$$

Also the core matrix $H_{\mu\mu}$ can be separated as follows:

$$\begin{aligned} H_{\mu\mu} &= (\mu | -\frac{1}{2} \nabla^2 - V_A | \mu) - \sum_{B(\neq A)} (\mu | V_B | \mu) \\ &= U_{\mu\mu} - \sum_{B(\neq A)} (\mu | V_B | \mu) \end{aligned} \quad (4.22)$$

$$H_{\mu\nu} = U_{\mu\nu} - \sum_{B(\neq A)} (\mu | V_B | \nu) \quad (\mu \neq \nu) \quad (4.23)$$

where $U_{\mu\mu}$ is the diagonal element of ϕ_{μ} with respect to the one-electron Hamiltonian containing only

the core of its own atom ($U_{\mu\mu}$ is an atomic quantity measuring the energy of the atomic orbital) and $U_{\mu\nu}$ is the one-electron matrix element using the local core Hamiltonian (μ and ν are on the

same atoms). It is noted that the cores consist of the nucleus and inner-shell electron.

Approximation D

The interaction terms of the distribution $\phi_\mu \phi_\nu$ on atom A and the nucleus of atom B, $(\mu | V_B | \nu)$ are equal to zero if $\mu \neq \nu$. The integrals $(\mu | V_B | \nu)$ are taken to be the same for all valence atomic orbitals on Atom A and there results

$$V_{AB} = (\mu | V_B | \mu) \quad (4.24)$$

It should be noted that the attraction term matrix element V_{AB} between nucleus B and the adjacent valence electron μ in the field of the nucleus A need not be symmetric. Therefore the equations (4.22) and (4.23) can be rewritten

$$H_{\mu\mu} = U_{\mu\mu} - \sum_{B(\neq A)} V_{AB} (\mu \text{ on atom } A) \quad (4.25)$$

$$H_{\mu\nu} = 0 \quad (\mu \neq \nu; \text{ both on the same atom}) \quad (4.26)$$

It is noted that $H_{\mu\nu} \neq 0$ if ϕ_μ and ϕ_ν are on different atoms which will be discussed in the next approximation.

Approximation E

If ϕ_μ and ϕ_ν are on different atoms, it is only necessary to consider the possible lowering of energy levels by being in the electrostatic field of two atoms simultaneously which is referred to as a "Resonance Integral" and is denoted by $\beta_{\mu\nu}$. $H_{\mu\nu}$ can be

approximated as

$$H_{\mu\nu} \cong \beta_{\mu\nu} = \beta_{AB}^0 S_{\mu\nu} \quad (4.27)$$

where β_{AB}^0 is a parameter depending only on the nature of the atoms A and B. Empirical values will be used for these parameters.

The $F_{\mu\nu}$ matrix elements now reduce to the form from equation (4.19) to (4.27)

$$F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - \frac{1}{2} P_{\mu\mu}) \chi_{AA} + \sum_{B(\neq A)} (P_{BB} \chi_{AB} - V_{AB}) \quad (4.28)$$

$$F_{\mu\nu} = \beta_{AB}^0 S_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \chi_{AB} \quad (\mu \neq \nu) \quad (4.29)$$

where ϕ_{μ} belongs to atom A and ϕ_{ν} belongs to atom B.

Using the same approximations, the total energy is given by one or two atom types from the equation (4.8)

$$E_{\text{total}} = \sum_A E_A + \sum_{A < B} E_{AB}$$

Where

$$E_A = \sum_{\mu}^A P_{\mu\mu} U_{\mu\mu} + \frac{1}{2} \sum_{\mu}^A \sum_{\nu}^A (P_{\mu\mu} P_{\nu\nu} - \frac{1}{2} P_{\mu\nu}^2) \chi_{AA} \quad (4.30)$$

$$E_{AB} = \sum_{\mu}^A \sum_{\nu}^B (2 P_{\mu\nu} \beta_{\mu\nu} - \frac{1}{2} P_{\mu\nu}^2 \chi_{AB}) + \left(\frac{Z_A Z_B}{R_{AB}} + P_{AA} P_{BB} \chi_{AB} - P_{AA} V_{AB} - P_{BB} V_{BA} \right) \quad (4.31)$$

IV-3. Choice of Parameters of CNDO1 and CNDO2

In the complete neglect of differential overlap approximation, the CNDO1 and CNDO2 methods are different levels of approximation of the equations.

The LCAOSCF Hatree-Fock matrix elements are

$$F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - \frac{1}{2}P_{\mu\mu})\gamma_{AA} + \sum_{B(\neq A)} (P_{BB}\gamma_{AB} - V_{AB}) \quad (4.28)$$

$$F_{\mu\nu} = \beta_{AB}^{\circ} S_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{AB} \quad (\mu \neq \nu) \quad (4.29)$$

where the bonding parameter β_{AB}° is given by

$$\beta_{AB}^{\circ} = 0.5 (\beta_A^{\circ} + \beta_B^{\circ}) \quad (4.32)$$

In the equation (4.32), β_A° is chosen empirically but depends only on the nature of atom A. These values are listed in Table 2. The parameters $U_{2s,2s}$ and $U_{2p,2p}$ can be estimated from ionization potentials, using the theoretical value of γ_{xx} (12).

$$\begin{aligned} I_s(X, 2s^m 2p^n) &= E(X^+, 2s^{m-1} 2p^n) - E(X, 2s^m 2p^n) \\ &= -U_{2s,2s} - (m+n-1)\gamma_{xx} \end{aligned} \quad (4.33)$$

$$\begin{aligned} I_p(X, 2s^m 2p^n) &= E(X^+, 2s^m 2p^{n-1}) - E(X, 2s^m 2p^n) \\ &= -U_{2p,2p} - (m+n-1)\gamma_{xx} \end{aligned} \quad (4.34)$$

or

$$-I_{\mu} = U_{\mu\mu} + (Z_A - 1)\gamma_{AA} \quad (4.35)$$

and the atomic electron affinities $A_{\mu}'s$ are used by the formula

$$-A_{\mu} = U_{\mu\mu} + Z_A \gamma_{AA} \quad (4.36)$$

Also the equation (4.28) can be rewritten

$$\begin{aligned}
 F_{\mu\mu} = & U_{\mu\mu} + (P_{AA} - \frac{1}{2}P_{\mu\mu}) \gamma_{AA} \\
 & + \sum_{B(\neq A)} (P_{BB} - Z_B) \gamma_{AB} \\
 & + \sum_{B(\neq A)} (Z_B \gamma_{AB} - V_{AB})
 \end{aligned} \tag{4.28}'$$

where the last term of equation (4.28)' is described as penetration integral contributions to $F_{\mu\mu}$.

The following table gives the approximate form between CND01 and CND02.

TABLE 4		
Difference between CND01 and CND02		
reference	CND01	CND02
$-U_{\mu\mu}$	$I_{\mu} + (Z_A - 1) \gamma_{AA}$	$\frac{1}{2}(I_{\mu} + A_{\mu}) + (Z_A - \frac{1}{2}) \gamma_{AA}$
		(4.37)
$F_{\mu\mu}$	$U_{\mu\mu} + (P_{AA} - \frac{1}{2}P_{\mu\mu}) \gamma_{AA}$	$U_{\mu\mu} + (P_{AA} - \frac{1}{2}P_{\mu\mu}) \gamma_{AA}$
	$+ \sum_{B(\neq A)} (P_{BB} \gamma_{AB} - V_{AB})$	$+ \sum_{B(\neq A)} (P_{BB} - Z_B) \gamma_{AB}$
		(4.38)
Where 1 the average ionization potentials I_{μ} (e.v.) used to fix $U_{\mu\mu}$ are listed in Table 3.		
2 the matrix elements $\frac{1}{2}(I_s + A_s)$ and $\frac{1}{2}(I_p + A_p)$ are listed in Table 5.		

TABLE 5								
Matrix Elements From Atomic Data (e.v.)								
	H	Li	Be	B	C	N	O	F
$\frac{1}{2}(I_a + A_a)$	7.176	3.106	5.946	9.594	14.051	19.316	25.390	32.272
$\frac{1}{2}(I_p + A_p)$		1.258	2.563	4.001	5.572	7.275	9.111	11.080

If the penetration integral term in equation (4.28)' was neglected to avoid the excess bonding and high value of force constants, then equation (4.28)' can be reduced to the form of (4.38). This corresponds to substituting the following term for CNDO2 from CNDO1:

$$V_{AB} = Z_B \chi_{AB} \quad (4.39)$$

Using parameters specified in the above way, the LCAOSCF equations are solved in the following steps:

- (a) An initial set of M.O. coefficients $C_{\lambda\mu}$ is obtained from a "Hückel type" calculation such that $F_{\mu\mu}$ is replaced by average ionization potential and $F_{\mu\nu}$ by $\beta^0 S_{\mu\nu}$.
- (b) Electrons are assigned in pairs to the M.O.'s with lowest energies.
- (c) Calculated $P_{\mu\mu}$ and $P_{\mu\nu}$ are used to form a new Hatree Fock matrix element $F_{\mu\nu}$.
- (d) New coefficients $C_{\lambda\mu}'$ are derived from this $F_{\mu\nu}$ and the process is repeated from step (b) until self-consistency is achieved on all coefficients with a tolerance of 0.0001.

V. Discussion of Results

The molecules selected for these calculations are as follows:

Hydrogen molecule (H_2), Lithium molecule (Li_2), Beryllium (Be_2), Nitrogen molecule (N_2), Fluorine molecule (F_2), water molecule (H_2O), Ammonia molecule (NH_3), Ethane molecule (C_2H_6), oxygen difluoride (F_2O), Difluorodiazine (N_2F_2), Methane (CH_4), Methylfluoride (CH_3F) and Hydrogen Peroxide (H_2O_2). These calculations will show the minimum configurations for bond lengths, bond angles, force constants, the

energy level considerations for NH_3 and F_2O , and the Barrier for NH_3 , C_2H_6 , N_2F_2 and H_2O_2 . Finally the calculations will extend the variation of parameters to fit the experimental potential surfaces.

V-1. Comparison of the equilibrium configurations and force constants

The ASCFT calculations with various inter-nuclear distances and bond angles are useful in predicting equilibrium bond lengths and bond angles. These results are listed in Table 6. The equilibrium configurations (bond lengths and bond angles) are in fairly good agreement with experimental values but the force constants are too high compared with the experimental values by a factor of about 2.0. This can be improved by adjusting parameters, such as the Slater exponent and θ° .

Sample results are discussed in Section V-9.

TABLE 6						
Comparison of Bond Lengths, Bond Angles & Force Constants (k_r & k_θ)						
	Bond Length (\AA) ⁽¹³⁾		Bond Angle (deg)		(13) Force Consts ($k_r: 10^5 \text{ dyne/cm}$ $k_\theta: 10^5 \text{ erg/rad}^2$)	
	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
H_2	0.7459	0.7415			10.143	5.6
N_2	1.1395	1.0976			52.160	23.10 (14)
H_2O	1.0289	0.958	104.22	104.45	17.260 0.845	8.23 0.694 (14)
NH_3	1.0657	1.015			14.68	6.86
			106.825	106.6	0.95	0.60 (14)
CH_4	1.1135	1.1135			12.65	5.45
			109.47	109.47		0.498 (15)
C_2H_6	R_{CH} 1.1195	1.102			12.12	5.35
D_3d	R_{CC} 1.4633	1.543			16.34	4.57
CH_3			107.76	109°37'		0.51 (16)
CCH			110.86	109°37'		0.63

V-2. Water molecules (H_2O)

For H_2O , C_{2v} symmetry was assumed with an O-H bond length of 0.96\AA . The first calculation shows an energy minimum at a bond angle of 107.28° . At this bond angle, the equilibrium O-H bond length of 1.0289\AA is obtained. With this bond length, the second calculation shows the bond angle of 104.22° at which the O-H bond length is calculated to be 1.0289\AA . This is in satisfactory agreement with the experimental bond angle of 104.45° (13). These calculations demonstrate the O-H bond stretching and angle HOH bending motion such that the O-H bond lengths tend to have symmetrical stretching motion and the bond angle tends to have scissoring motion (symmetrical in-plane deformation). A series of these calculations is listed in Table 7. The stretching force constant is calculated to be 17.26×10^5 (dyne/cm) which is higher by a factor of 2.1 with respect to the experimental value of 8.23×10^5 (dyne/cm). The bending force constant is calculated to be 0.845×10^{-11} (erg/rad²) which is higher by a factor of 1.22 than the experimental value of 0.694×10^{-11} (erg/rad²) (14).

TABLE 7			
	Calculation of R_{OH} and Calculation I	HOH for H_2O Calculation II	Experiment
$R_{\text{OH}}(\text{\AA})$	0.96 (Exp)	1.0280	0.958
$\angle \text{HOH}$	107.28	104.22	104.45
* The computer outputs (sample) are listed in Appendix 2.			

V-3. Ammonia Molecule (NH_3)

The ammonia molecule with an NH bond length of 1.05\AA (13) is calculated to be non-planar with an $\angle \text{HNH}$ bond angle of 106.825°

which is in close agreement with the experimental value of 106.6° (13). At this value of the bond angle, the NH bond length was found to be 1.0657 \AA . The subsequent calculation shows a bond angle of 104.86° and again the bond length of 1.0673 \AA . On the other hand the equilibrium bond length for the planar configuration gives 1.0543 \AA . It is interesting when calculations presented here are compared with results recently calculated by R. Moccia and L. Randaccio (17). They reported the minimum bond length of 1.878 a.u. (0.9938 \AA) at a bond angle of $105^\circ 36'$ and a bond length of 1.837 a.u. (0.9721 \AA) at a planar configuration. The change in minimum bond length between non-planar and planar configuration is 0.0217 \AA by Moccia and 0.0114 \AA by the ASCFT. The smaller value of this bond length change in the present calculation is due to the higher stretching force constants for ASCFT. Also, subsequent calculations can predict the symmetrical bond stretching motion and symmetrical in-plane deformation of bond angle for the ground state of this molecule. The stretching force constants are calculated to be $14.64 \times 10^5 \text{ (dyne/cm)}$. This differs by a factor of 2.14 with respect to the experimental value of $6.86 \times 10^5 \text{ dyne/cm}$ (14) and the bending force constants are calculated to be $0.95 \times 10^{-11} \text{ erg/rad}^2$ (factor of 1.58 with respect to experimental values of $0.6 \times 10^{-11} \text{ erg/rad}^2$ (14)).

It is also interesting to compare the barriers calculated by the several methods and the difference in barriers with respect to adjusting the various parameters. These are listed in Tables 8 and 9, respectively.

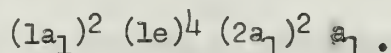
TABLE 8

Comparison of the results of Calculations for NH₃

Reference	Method of calculations	R _{NH} (a.u.)	∠HNH (deg)	Pyramid Height(a.u.)	Barrier Height(a.u.)
Present Calc.	Approximate (CNDO) SCF MO	1.9923	106°49'	0.749	0.0251
Higuchi (18)	Approximate polycenter SCF MO	1.916	108.0	0.592	0.0147
Kaplan (19)	Single Determinant polycenter SCF MO	1.916	106°47'	0.719	0.146
Moccia (20)	Single Determinant one center SCF MO	1.928	110°2'	0.6245	0.0027
Joshi (21)	Single determinant one center SCF MO	1.867	109°34'	0.626	0.0411
Moccia (17)		1.878	105°36'	0.739	0.00905
Experiment		1.9162	106°47'	0.719	0.0092 ⁽²²⁾

From Table 9, it is interesting to compare the change in barrier with respect to a change in bond angles at the fixed bond length of 1.0657Å (Calculation II and IV) such that the change in barrier is 0.000030279 a.u. (0.002540830 - 0.002510551) and the change in bond angle is 1.965° (106.825° - 104.86°). From this calculation, it is found that the calculated barrier is 0.002540830 a.u. which is different by only 1.2% from the first calculated barrier.

The electronic configuration is found to be



Configurations calculated by ASCFT, EHT and full LCAOSCT by H. D.

Joshi (21) are compared in Fig. 1 and Fig 2. There is complete agreement between ASCFT and full LCAOSCT calculations for the orbital energies as a function of height of pyramid. It is noted that the lowest orbital

FIG. 1. E_{tot} AND E_{orb} OF NH_3 AS FUNCTION OF PYRAMID HEIGHT.

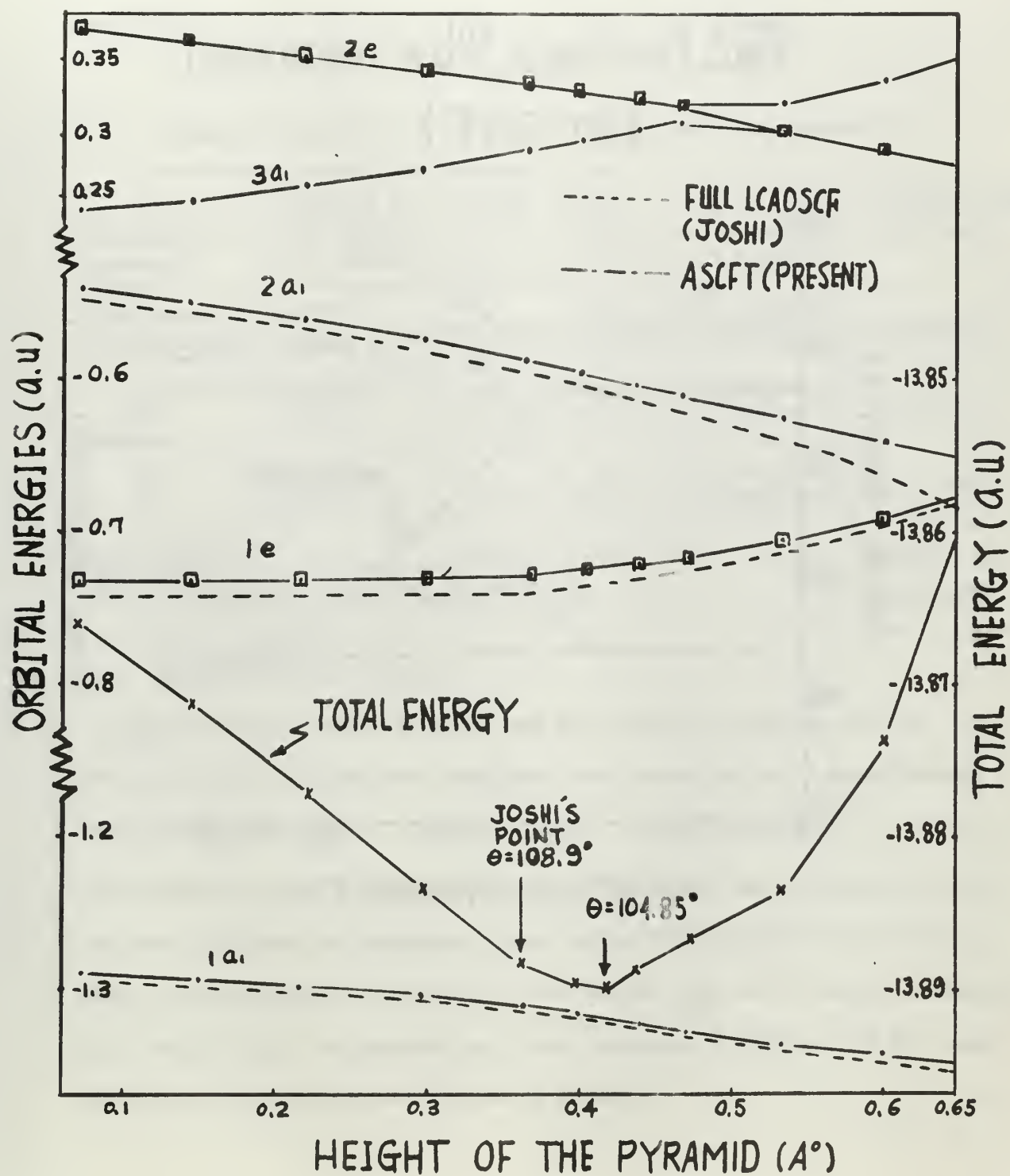
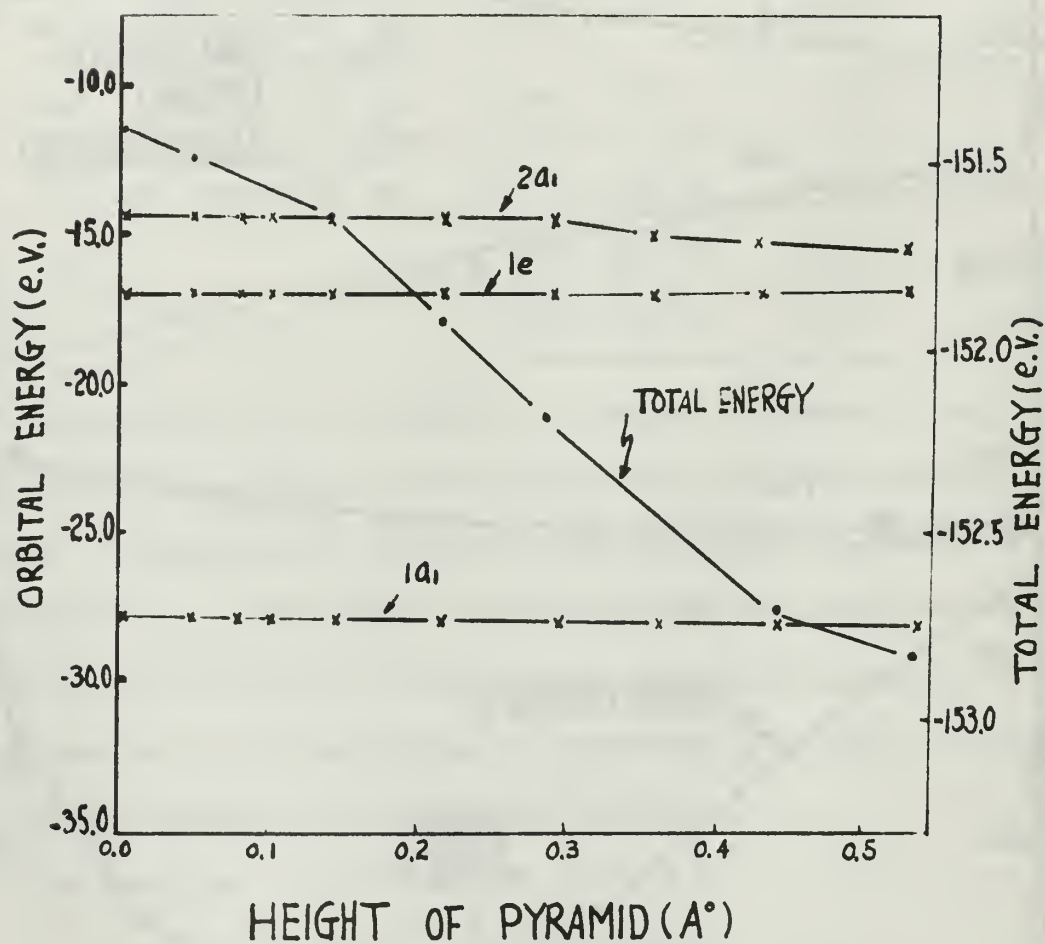


FIG.2. $E_{\text{tot.}}$ & $E_{\text{orb.}}$ OF NH_3 VS. PYRAMID HEIGHT
(BY EHT)



energy in LCAOSCFT calculation is due to the (1s) electron (inner-shell) of Nitrogen but ASCFT neglects that part. On the other hand, the EHT calculation (Fig. 2) does not even demonstrate a double minimum potential curve. Therefore the EHT is quite inferior for this kind of molecule.

TABLE 9					
Change in Barrier for NH ₃ w.r.t. minimizing the parameter					
	$R_{\overline{NH}}$ (A°)	$\angle ZNH$	$\angle HNH$	E_{total} (a.u.)	Barrier (a.u.)
Calculation I (General)	1.02 (fixed)	o	120	-13.85761125	0.02013903
	1.02 (fixed)	112.0	106.825	-13.87775028	
Calculation II (Equilibrium)	1.0543	o	120	-13.86430636	0.02510551
	1.0657	112.0	106.825	-13.88941245	
III	1.0543	o	120	-13.86430636	0.02453518
	1.0543	113.18	105.10	-13.88890154	
IV	1.0657	o	120	-13.86362706	0.02608760
	1.0657	113.55	104.86	-13.88971466	
Experimental		112.206	106.6		0.0092
* The true Barrier for this calculation is (13.88971466 - 13.86430636) (a.u.)					0.02540830

V-4. Ethane molecule (C₂H₆)

Calculations based on ASCFT and EHT have been carried out for Ethane in both eclipsed and staggered configurations with experimental values such that $R_{\overline{CC}} = 1.543A^\circ$, $R_{\overline{CH}} = 1.102A^\circ$ and $\angle CCH = 109^\circ 37'$ (tetrahedral angle). The first calculation shows the equilibrium angle for both eclipsed and staggered forms using EHT and ASCFT. The energy then was minimized by varying the bond length $R_{\overline{CC}}$, and finally by varying bond length $R_{\overline{CH}}$. The stretching force constants ($k_{\overline{CC}}$ and $k_{\overline{CH}}$) were found and those values are listed in Table 10.

It is of interest to look at the barrier resulting in the change in geometry. These changes in parameters and the corresponding barriers are compared in Table 11. These comparisons show that the eclipsed form is more open than the staggered form by a few tenths of a degree; also the bond length $R_{\overline{CC}}$ is elongated a few thousandths of an Ångström and the bond length $R_{\overline{CH}}$ is shortened a few ten thousandths of an Ångström. Some researchers have shown an elongation for $R_{\overline{CH}}$. Although these changes ($R_{\overline{CH}}$) in geometry are small, their effect on the internal-rotation barrier is very significant.

TABLE 10					
Comparison of Ethane Betn. EHT & ASCFT Calculation					
Reference	Calculated				Expt. (16) D3d
	ASCFT		EHT		
	Eclipsed	Stagger	Eclipsed	Stagger	
$\angle CCH$	111.28	110.86	110.99	110.44	109°37'
$\angle HCH$	107.60	108.04	107.90	108.48	109°37'
$R_{\overline{CC}}$	1.4660	1.4633	1.8070	1.8000	1.543
$R_{\overline{CH}}$	1.1193	1.1195	0.9086	0.9088	1.102
$k_{\angle CCH} [10^{11} \frac{\text{erg}}{\text{rad}^2}]$	(1.74)	(1.67)	(8.85)	(8.8)	0.63
$k_{\angle HCH} [10^{11} \frac{\text{erg}}{\text{rad}^2}]$	()	()	()	()	0.51
$k_{\overline{CC}} [10^5 \frac{\text{dyne}}{\text{cm}}]$	15.887	16.340	197.0	184.0	4.57
$k_{\overline{CH}} [10^5 \frac{\text{dyne}}{\text{cm}}]$	12.125	12.124	164.05	186.56	5.35
Barrier (kcal/mole)	2.3288		2.6586		2.875 ⁺ .125 -(23)

There is some uncertainty in the Table 11 for EHT calculation. Every reported calculation scheme has the same tendency to increase the barrier when the parameters are changed in sequence, but EHT

calculation shows the barrier is decreased. The resultant barrier by EHT is 1.6358 kcal/mole. This is not in agreement with the value 2.6586 kcal/mole found by varying only one parameter, $\angle CCH$, holding the other two parameters R_{CC} and R_{CH} constant. It is noted that R. Hoffmann (1) reported 4.0 kcal/mole with a Slater exponent (H) of 1.0. Present calculations use the value of 1.2. However the results are in fairly good agreement with experimental values using both ASCFT and EHT (with some uncertainty).

TABLE 11						
Comparison of Barrier for Ethane						
Reference	\triangle Parameter (Ecl. — Stag)			Barrier (Eclip. — Stag)		
	$\angle CCH$ (deg)	R_{CC} (A°)	R_{CH} (A°)	$\angle CCH$	R_{CC}	R_{CH}
T.L.Hill ⁽²⁴⁾ (1948)	0.34	0.0054	0.0002	0.613	0.665	0.700
L.S. Bartell ⁽²⁵⁾ (1960)	0.20	0.0029	0.0001	0.367	0.383	0.394
J.T.Vanderslice ⁽²⁶⁾ & E.A.Mason (1960)	0.17	0.0024	-0.0001	0.387	0.416	0.434
L.Salem ⁽²⁷⁾ (1962)	0.05	0.0007	0.0000	0.104	0.106	0.107
K.E.Howlett ⁽²⁸⁾ (1960)	0.40	0.0059	-0.0002	0.779	1.108	1.298
V.Magnasco ⁽²⁹⁾ (1962)	0.55	0.0080	-0.0011	-1.532	1.675	2.944
O.J.Sovers & ⁽³⁰⁾ M.Karplus (1966)	0.20	0.0029		2.311	3.611	
Present (ASCFT)	0.42	0.0027	-0.0002	1.8637	2.2848	2.3288
(EHT)	0.55	0.0070	-0.0002	2.6586	1.5746	1.6358
Expt.	3.03 ± 0.3 (kcal/mole) (31)			2.875 ± 0.125 (kcal/mole) (23)		

V-5. Methane (CH_4) and Methylfluoride (CH_3F)

Calculations between methane and methylfluoride were carried out using tetrahedral symmetry for methane and C_{3v} symmetry for methylfluoride with $R_{\text{CH}} = 1.1135\text{\AA}$ for CH_4 and $R_{\text{CH}} = 1.109$ and $R_{\text{CF}} = 1.385$ for CH_3F . The calculated values for the equilibrium configurations are listed in Table 12. The force constants are calculated for each molecule and these are listed in Table 12. The stretching force constants are different by a factor of 2.3 for CH_4 and 2.5 for CH_3F with respect to their observed values (15).

For a methane molecule, the calculated bond lengths and bond angles are the same as the observed values.

For methylfluoride molecules, the bond angle $\angle\text{HCH}$ is more open than the angle of $\angle\text{HCF}$ which can be explained as follows: there exists rehybridization for the CH_3F molecule because there must be more P-character in C-F bond due to the electron withdrawing fluorine; on the other hand, there must be more S-character in C-H bond which gives more SP^2 hybrid character for the C-H sigma (σ) bonds. It is obvious that the SP^2 hybrid orbital is more planar than SP^3 . Therefore $\angle\text{HCH}$ is more open. It is here that the best agreement between theoretical and calculated results was found.

TABLE 12						
Comparison of r , θ and k_r & k_θ between CH_4 & CH_3F						
CH_4	Bond Length (\AA)		Bond Angle (deg)		Force Consts.	
	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
	1.1135	1.1135			12.65	5.45
			109.47	109.47	(.745)	0.498
R_{CH}	1.1180	1.109			12.09	4.71(15)
R_{CF}	1.3458	1.385			23.57	5.64(15)
CH_3F $\angle\text{HCH}$			110.382	109.997		0.443(15)
$\angle\text{FCH}$			108.54	108.94	(1.77)	0.792(15)

V-6. Difluorodiazine (N_2F_2)

Calculations have been carried out for difluorodiazine in both trans and Cis configurations with $R_{\text{NN}} = 1.25\text{\AA}$, $R_{\text{NF}} = 1.44\text{\AA}$ and $\angle\text{NNF} = 115^\circ$ (13). In both configurations, the new equilibrium distances and bond angles are determined and are listed in Table 14. When comparisons are made of the equilibrium geometry in Table 14, the bond angle $\angle\text{NNF}$ is more open for Cis than trans configurations. Significantly, the bond length R_{NN} is elongated a few thousandths more for trans than Cis (same for R_{NF}).

It is of interest to compare the energy level difference between Cis and trans configurations. The experimental results giving the stability between both configurations are listed in Table 13. In 1963, Armstrong and Marantz published that the Cis form is more stable by 3.0 ± 0.3 kcal/mole (36) (refer also (37)). The present calculation predicts the Cis form to be more stable by 3.249 kcal/mole than the trans (C_{2h}) form. Fortunately, these results are in most satisfactory

agreement with experimental value. In Table 14 are compared the differences in energies between the Cis and trans configurations for a variation in molecular parameters. First the angle $\angle \text{NNF}$ was varied to minimize the energy. With this bond angle, the minimum bond length R_{NN} was calculated and finally the minimum bond length R_{NF} was found. In each case, the difference in energies was compared with the one obtained initially. It was found that there is no effect due to varying the angle $\angle \text{NNF}$ and bond length R_{NN} but there is a very significant difference when the bond length R_{NF} was minimized. This result shows the configuration is affected significantly due to the R_{NF} stretching motion.

TABLE 13			
Results of experiments for N_2F_2 (stability)			
Year	Author	Reference	Results
1947	S.H. Bauer ⁽³²⁾	J. Am. Chem. Soc., 69, 3104	trans is more stable than Cis configuration
1959	C.B. Colburn, et. al. ⁽³⁵⁾	" " " " , 81, 205	
1960	R.H. Sanborn ⁽³⁴⁾	J. Chem. Phys., 33, 1855	Cis and $\text{N}=\text{N}<\text{F}$ is more chemically active isomer
1961	R. Ettinger, et. al. ⁽³⁵⁾	" " " " , 34, 2187	
1963	G.T. Armstrong ⁽³⁶⁾ & S. Marantz	J. Chem. Phys., 38, 169	Cis is more stable by 3.0 ± 0.3 kcal/mole
Present			Cis is more stable by 3.249 kcal/mole

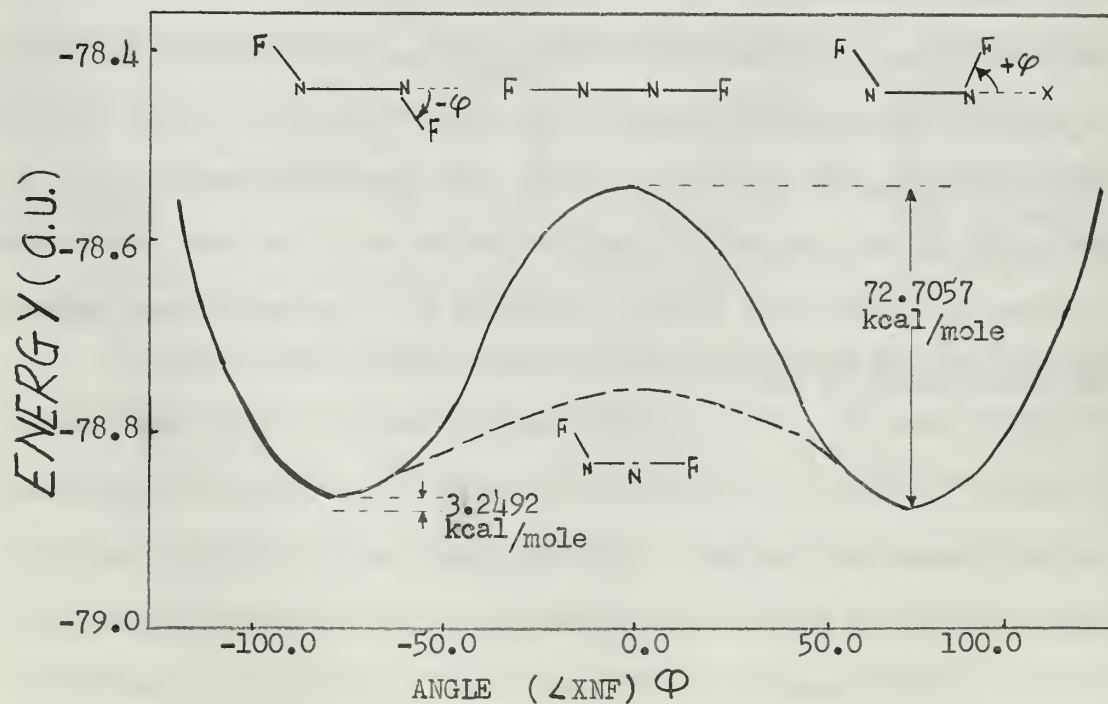
The next interesting calculation is the barrier due to the rotational motion which was reported by the Binenboyn (37) . It was reported by experiment to be 32.0 kcal/mole and calculated to be 84 kcal/mole (36) between trans and linear configuration. However, the present calculations were carried out in various ways and those results are listed in Table 15. The calculated barrier between linear and trans form in

TABLE 14							
Equilibrium Configuration Btn. C_{2v} & C_{2h} for N_2F_2							
Calculation	Parameters			Δ Par(C_{2v} - C_{2h})			Diff. in Barrier
	$\angle NNF$ (deg)	R_{NN} (A°)	R_{NF} (A°)	$\angle NNF$	R_{NN}	R_{NF}	$\Delta E(C_{2v}-C_{2h})$
I General	115	1.25	1.44	0	0	0	0.2553(0)
	115	1.25	1.44				
II C_{2v} C_{2h}	109.98	1.25	1.44	5.89	0	0	0.2553(0)
	104.09	1.25	1.25				
III C_{2v} C_{2h}	109.98	1.2197	1.25	5.89	-0.0021	0	(-)0.04962 (.31)
	104.09	1.2218	1.25				
IV C_{2v} C_{2h}	109.98	1.2197	1.2410	5.89	-0.0021	-0.0031	(-)3.2492 (3.5)
	104.09	1.2218	1.2441				
Expt. value							(-)3.0±0.3

Table 15 is too high with respect to the reported barrier but the calculation between trans and C_2 form shows a satisfactory agreement with the calculated (38) and experimental value (39). It must be noted that when an attempt was made to calculate the rotational barrier, no dihedral angle exists; that is, when the dihedral angle is 90 degrees, the bond angle $\angle NNF$ turns out linear, and also the dihedral angle does not exist and the motion is predicted to be an up and down motion which is shown in Calculation IV and V in Table 15. The calculated barriers are illustrated in Fig. 3.

TABLE 15					
Comparison of Barrier for N_2F_2					
No.	Ref.	Parameters			Etot. (a.u.)
		$\angle NNF$	R_{N-N}	R_{N-F}	
I	C2v (Cis)	109.98	1.2197	1.2410	-78.87407234
II	C2h (trans)	104.09	1.2218	1.2441	-78.86889607
III	0.5(I + II)	107.035	1.22075	1.24255	-78.87148421
IV	C2 (_ _)	114.07	1.2208	1.2426	-78.75824577
V	C _{2v} (---)	180.0	1.2119	1.440*	-78.54333813
Barrier	E(II) - E(IV) = 69.456	E(II) - E(IV) = 204.356	E(I) - E(IV) = 72.7057	E(I) - E(V) = 207.657	kcal/mole
Exp. E(II) -- E(V) = 32 kcal/mole (37)					
Cal. E(II) -- E(V) = 84 kcal/mole (36)					

Fig. 3 Barrier for N_2F_2 as function of $\angle XNF$

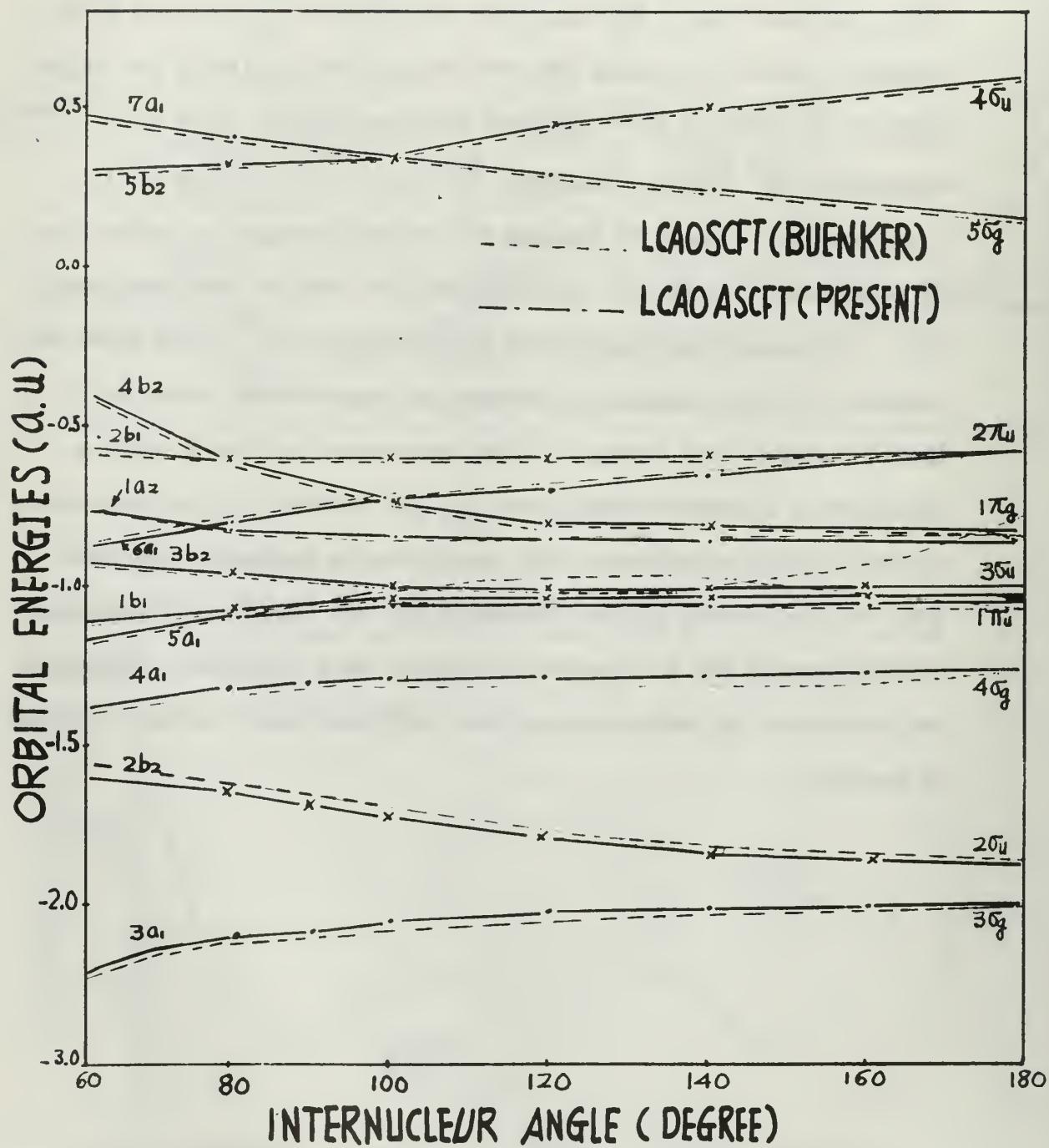


V-7. Oxygen difluoride (F_2O)

For the F_2O molecule with C_{2v} symmetry ($R_{\text{OF}} = 1.41\text{\AA}$ (13)), the lowest energy configuration is calculated to be bent with an $\angle\text{FOF} = 97.16^\circ$ (at fixed $R_{\text{OF}} = 1.50\text{\AA}$) as compared with the experimental angle of 103.8° (38). The bond length R_{OF} (at angle of 97.16°) is calculated to be 1.1792\AA . Also the bending and stretching force constants are calculated to be 1.1497×10^{-11} erg/rad² (observed $K_{\angle\text{FOF}} = 0.55 \times 10^{-11}$ erg/rad²) and 40.94×10^5 dyne/cm (observed $K_{\text{OF}} = 5.57 \times 10^5$ dyne/cm (14)).

It is of interest to compare the orbital energies as a function of internuclear angle with that published by Buenker and Peyerimhoff (39). The calculated results are illustrated in Fig. 4 and these were compared with calculations by Buenker and Peyerimhoff (using full LCAOSCF theory) also in Fig. 4. The comparison in Fig. 4 shows a satisfactory agreement except for $5a_1$, $1b_1$ and $3b_2$. It is noted that, in full LCAOSCF calculation, the lowest doubly degenerate orbitals (due to $1s$ electrons of two Fluorines) and the next singly degenerate orbital (due to the $1s$ electron of Oxygen) were neglected. Therefore the comparison is valid starting with the third level in the Fig given by Buenker.

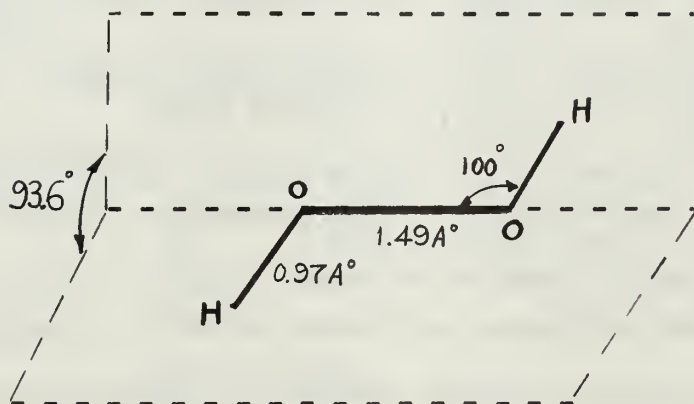
FIG. 4. ORBITAL ENERGY OF F_2O AS FUNCTION OF $\angle FOF$.



V-8. Hydrogen Peroxide (H_2O_2)

For the hydrogen peroxide molecule, the calculations were performed to find the barrier and the equilibrium configurations with $R_{\text{OH}}=0.97\text{\AA}$, $\angle\text{HOO}=100^\circ$, $R_{\text{OO}}=1.49\text{\AA}$ and dihedral angle of 93.6° (13). Unfortunately, the present calculation does not show the existence of a dihedral angle. The result of the calculation shows that there exists a Cis and trans configuration for H_2O_2 just as for N_2F_2 . The structural parameters are illustrated in Fig. 5.

Fig. 5 Structural Parameters (H_2O_2)



V-9. Homonuclear diatomic molecules

For the diatomic molecules, the equilibrium configurations of H₂, Li₂, N₂ and F₂ were calculated. An attempt was made to find a new set of optimized parameters by changing the Slater exponents and beta zeroes (β°). The equilibrium bond lengths and force constants are listed in Table 16. It is noted that B₂, C₂ and O₂ molecules are excluded in the calculations because they are ground state triplets, and the Be₂ molecule is non-bonded. The necessary partial derivatives were found and listed in Table 16.

TABLE 16								
Equilibrium Configurations and Some Partial derivatives for homo nuclear diatomic molecules								
	Re (A°)		Kr (10 ⁵ dyne/cm)		average partial between (S.E.) ± 0.1 and also $\beta^\circ \pm 1.0$			
	Cal.	Obs.	Cal.	Obs.	$(\partial R/\partial \beta^\circ)_S$	$(\partial R/\partial \beta^\circ)_S$	$(\partial Kr/\partial \beta^\circ)_S$	$(\partial Kr/\partial \beta^\circ)_S$
H ₂	0.746 (0.89)	0.74	10.14 (6.5)	5.6	-0.54	-0.34	19.18	1.0555
Li ₂	2.179 (2.789)	2.67	0.84 (0.41)	0.25	-2.94	-0.022	3.07	0.52
N ₂	1.14	1.09	52.16	23.10	-0.47	-0.01	61.06	2.34
F ₂	1.12	1.44	56.41	4.45				

For those molecules, an attempt was made to find a new set of optimized parameters fitting experimental equilibrium bond lengths and force constants. The Slater exponent and β° were considered in adjusting the parameters to optimize agreement for calculated potential surfaces. The procedures used to find a new set of Slater exponents and beta zero (β°) were as follows:

First: Change the Slater exponent by ± 0.1 and beta zero by ± 1.0 ,

then find the calculated equilibrium bond length and force constant.

Second: Find the partial derivatives

$$\left(\frac{\partial R}{\partial S}\right)_{\beta^0}, \left(\frac{\partial R}{\partial \beta^0}\right)_{\beta^0}, \left(\frac{\partial R}{\partial S}\right)_S \text{ and } \left(\frac{\partial R}{\partial \beta^0}\right)_S$$

where "S", stands for Slater exponent.

Third: Find the new Slater exponent and by following equations:

$$dR = \left(\frac{\partial R}{\partial S}\right)_{\beta^0} dS + \left(\frac{\partial R}{\partial \beta^0}\right)_S d\beta^0 \quad (5.1)$$

$$dR = \left(\frac{\partial R}{\partial S}\right)_{\beta^0} dS + \left(\frac{\partial R}{\partial \beta^0}\right)_S d\beta^0 \quad (5.2)$$

then approximate the dR, dS and $d\beta^0$ as follows:

$$dR \approx \Delta R = R_{\text{eq.}} - R_{\text{cal.}}$$

$$dS \approx \Delta S = S_{\text{new}} - S_{\text{cal.}}$$

$$d\beta^0 \approx \Delta \beta^0 = \beta_{\text{new}}^0 - \beta_{\text{cal.}}^0 \quad (5.3)$$

Fourth: Solve equation (5.1) and (5.2) to find the new Slater exponent and β^0 . For example:

(1) H_2 molecule:

$$\begin{bmatrix} -0.06 \\ -4.83 \end{bmatrix} = \begin{bmatrix} -5.4 & -3.4 \\ 19.18 & 1.055 \end{bmatrix} \rightarrow \begin{bmatrix} -0.277 \\ 0.457 \end{bmatrix} = \begin{bmatrix} \Delta S \\ \Delta \beta^0 \end{bmatrix}$$

therefore

$$\begin{aligned} S_{\text{new}} &= 0.923 \\ \beta_{\text{new}}^0 &= 9.457 \end{aligned} \quad (5.4)$$

(2) Li_2 case:

$$\begin{bmatrix} -0.49 \\ -0.59 \end{bmatrix} = \begin{bmatrix} 2.94 & 0.022 \\ 3.07 & 0.52 \end{bmatrix} \rightarrow \begin{bmatrix} -0.164 \\ -0.410 \end{bmatrix} = \begin{bmatrix} \Delta S \\ \Delta \beta^0 \end{bmatrix}$$

therefore

$$\begin{aligned} S_{\text{new}} &= 0.49 \\ \beta_{\text{new}}^0 &= 8.59 \end{aligned} \quad (5.5)$$

(3) N_2 case:

$$\begin{bmatrix} -0.05 \\ -29.06 \end{bmatrix} = \begin{bmatrix} -0.47 & -0.01 \\ 61.06 & 2.34 \end{bmatrix} \rightarrow \begin{bmatrix} 0.87 \\ -35.5 \end{bmatrix} = \begin{bmatrix} \Delta S \\ \Delta \beta^0 \end{bmatrix}$$

therefore

$$\begin{aligned} S_{\text{new}} &= 2.87 \\ \beta_{\text{new}}^0 &= -9.5 \end{aligned} \quad (5.6)$$

From these results, (5.4) and (5.5) are consistent but (5.6) is completely inconsistent because the force constant is too high.

Fifth: Finally, repeat the calculation using the above new set of input parameters (S_{new} and $\beta^{\circ}_{\text{new}}$). The result for the H_2 and Li_2 molecules are listed in parentheses in Table 16.

VI. CONCLUSION

The Approximate Self-Consistent Field M.O. theory was applied to the calculation of electronic structure for several selected molecules and these results were compared with results by full LCAOSCFT calculations, if they were available. The most important features of these calculations are to predict equilibrium configurations (bond length and bond angle) and the barrier by the variation of internuclear distances and angles using the ASCFT. The EHT calculations are limited to hydrocarbons which give good results (refer to calculation of Ethane molecule). In general, the barrier predicted by ASCFT calculation is in satisfactory agreement with the experimental value.

An attempt was made to find a new set of input parameters (Slater exponent and β°) to improve the prediction of potential surfaces for certain homonuclear diatomic molecules but the attempt failed except for the H_2 and Li_2 molecules (see Table 16).

The features of Potential Surfaces of molecules can be predicted with the approximate self-consistent field theory. Qualitatively, the agreement between calculations and experimental observations is quite good. It is conceivable that, with the adjustment of certain parameters

such as resonance integrals (β^0), Slater exponents and penetration integrals, quantitative agreement with experimental results can be obtained.

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APPENDIX

- I Computer program for Approximate Self-Consistent Field Theory (ASCFT)

```

-COUP,, YON BOX 41 3/13/25,20,0000.
-FTN,E,L,P.

PROGRAM DUMMY
  DIMENSION IPT(5), Z(18), ZS(18), BETA(40), U(40), COORD(3,18),
  1F(4,40), S(40,40), C(40,40), P(40,40), COS(3,18,18), PA(18),
  2V(18,18), G(18,18), E(18,18), RAD(18,18), RHO(18,18), TAU(18,18),
  3ISTP(18), AL(18), TH(18), PH(18), BOND(18), AW(18),
  4PP(40,40), PB(18)

C THIS IS A DUMMY PROGRAM WHICH FIRST CALLS FOR INPUT DATA AND
C THEN PERFORMS THE CNDO OPERATIONS
  1 CALL INPUT(N,NH,NO,IPT,ISTP,AL,TH,PH,BOND,Z,ZS,BETA,U,COORD,AW)
  CALL CNDO (N,NH,NO,IPT,Z,ZS,BETA,U,COORD,F,S,C,P,COS,PA,V,G,E,ET,
  1RAD,RHO,TAU,PP,PB)
  GO TO 1
END

SUBROUTINE CNDO (N,NH,NO,IPT,Z,ZS,BETA,U,COORD,F,S,C,P,COS,PA,V,
1G,E,ET,RAD,RHO,TAU,PP,PB)
  DIMENSION IPT(5), Z(18), ZS(18), BETA(40), U(40), COORD(3,18),
  1F(4,40), S(40,40), C(40,40), P(40,40), COS(3,18,18), PA(18),
  2V(18,18), G(18,18), E(18,18), RAD(18,18), RHO(18,18), TAU(18,18),
  3PP(40,40), PB(18)

C N IS THE NUMBER OF ATOMS IN THE MOLECULE
C NH IS THE NUMBER OF HYDROGEN ATOMS IN THE MOLECULE
C NO IS THE NUMBER OF ORBITALS WHICH OCCUPY ELECTRONS
C IPT(1) = 1 IF COORDINATES, DIRECTION COSINES, THE DISTANCE MATRIX,
C THE RHO MATRIX, THE TAU MATRIX, THE OVERLAP MATRIX, THE F MATRIX,
C THE GAMMA MATRIX, AND THE V MATRIX IS TO BE PRINTED OUT. IF NO
C PRINT OUT OF THESE IS DESIRED, SET IPT(1) = 0
C FOR IPT(1) GREATER THAN 1, SUCCESSIVE PRINTOUTS WILL OCCUR, DETAILING
C THE ITERATION PROCESS FOR EACH ITERATION
C IPT(2) IS NOT USED
C IPT(3) SET THIS = 0 FOR A CLOSED SHELL MOLECULE. IF IPT(3) = 1,
C ONE ELECTRON WILL BE REMOVED FROM HIGHEST OCCUPIED ORBITAL (RADICAL),
C IF IPT(3) = 2, A CNDO/2 CALCULATION WILL BE FOR SEPARATE MATRICES
C FOR ALPHA AND BETA SPINS (FOR FREE RADICALS AGAIN).
C IPT(4) = 1 FOR CNDO/1 CALCULATIONS, AND = 2 FOR CNDO/2 CALCULATIONS.

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C IF(5) IS THE MAXIMUM NUMBER OF ITERATIONS THE PROGRAM WILL PERFORM
C BEFORE QUITTING. TYPICALLY THIS IS ABOUT 20.
C Z IS THE ARRAY OF CHARGES ON THE CORE
C ZS IS THE ARRAY OF SLATER EXPONENTS.
C BETA IS THE ARRAY OF BETA ZEROS.
C U IS THE ARRAY OF IONIZATION POTENTIALS.
C COORD IS THE MATRIX OF CARTESIAN COORDINATES.
C F IS THE F MATRIX.
C C IS THE MATRIX OF EIGENVECTORS.
C P IS THE BOND ORDER, CHARGE DENSITY MATRIX.
C COS IS THE DIRECTION COSINE MATRIX.
C PA IS THE ARRAY OF ELECTRON CHARGE DENSITIES FOR EACH ATOM.
C V IS THE V-INTEGRAL MATRIX.
C G IS THE MATRIX OF GAMMA INTEGRALS.
C E IS THE ENERGY OF THE MOLECULE.
C ET IS THE ENERGY MATRIX, BREAKING DOWN THE ENERGY INTO ATOMIC
C AND INTERACTION TERMS.
C RAD IS THE INTERATOMIC DISTANCES MATRIX.
C RHO IS THE RHO MATRIX.
C TAU IS THE TAU MATRIX.
C PP AND PB ARE ARRAYS USED FOR OPEN SHELL CALCULATIONS ANALAGOUS TO
C P AND PA IN THE CLOSED SHELL CALCULATION.
C THE SUBROUTINES HAVE THE FOLLOWING FUNCTIONS
C FULLY HANDS PRELIMINARY CALCULATIONS, CONVERTING THE COORDINATE
C MATRIX AND THE SLATER DETERMINANT MATRIX INTO COS, RAD, RHO,
C TAU.
C OVERL SETS UP THE OVERLAP MATRIX GIVEN ZS, COORD, COS, RAD, RHO, AND
C TAU.
C GVAD SETS UP G AND V USING ZS, RAD, RHO, TAU, Z, AND IPT.
C INITL SETS UP THE INITIAL F MATRIX TO BE DIAGONALIZED.
C FIRST PRINTS OUR COORD, COS, RAD, RHO, TAU, S, F, G, AND V.
C HDIAG DIAGONALIZES F, GIVING EIGENVECTORS C
C PM SETS UP THE P AND PA MATRIX GIVEN C, NO, AND IPT(3).
C SETF SETS UP THE F MATRIX IN TERMS OF THE C OBTAINED ON PREVIOUS IT.
C INTER PRINTS OUT C, P, PA, AND F.
C COMPR SETS KEY = 0 IF C AND P MATRIX ELEMENTS AGREE TO WITHIN .0001.

```


C ENRGY CALCULATES THE ENERGY ELEMENTS AFTER ITERATION IS COMPLETE.

```

      NT = 4*(N-NH)+NH
      CALL PREL(N,COORD,COS,RAD,ZS,RHO,TAU,M)
      CALL OVERL(N,NH,ZS,COORD,COS,RAD,S,RHO,TAU)
      CALL GVAR(N,NH,ZS,RAD,G,V,RHO,TAU,Z,IPT)
      CALL INITL(N,NH,BETA,U,S,F)
      IF(IPT(1)) 4,5,4
4     CALL FRST(N,NH,COORD,COS,RAD,RHO,TAU,S,F,G,V)
5     CONTINUE
      CALL HDIAG(F,C,U,NT,INR)
      NUC = IPT(5)
      IF(IPT(3)/2-1) 6,6,6
6     DO 20 I = 1,NUC
          CALL PM(N,NH,NO,C,P,PA,IPT(3))
          CALL SETF(N,NH,P,PA,G,V,BETA,S,Z,F,U,IPT)
          IF(IPT(1)-I) 15,15,14
14     WRITE (51,101)
          WRITE (51,100) (F(J,J), J = 1,NT)
          CALL INTLR(N,NH,C,P,PA,F)
15     CONTINUE
          DO 16 J = 1,NT
              DO 16 K = 1,NT
16         PP(J,K)=P(J,K)
              CALL HDIAG(F,C,U,NT,INR)
              CALL PM(N,NH,NO,C,P,PA,IPT(3))
              CALL COMPR(N,NH,P,PP,KEY)
              IF(KEY) 20,30,20
20     CONTINUE
30     CONTINUE
          WRITE (51,101)
          WRITE (51,100) (F(J,J), J = 1,NT)
          CALL SETF(N,NH,P,PA,G,V,BETA,S,Z,F,U,IPT)
          CALL INTER(N,NH,C,P,PA,F)
35     WRITE (51,104)
          CALL ENRGY(N,NH,P,J,G,BETA,S,Z,RAD,PA,E,ET,V,IPT)
          IF(IPT(1)+1) 39,41,39

```

```

39 DO 40 J = 1,N
40 WRITE (51,100) (E(J,K), K = J,N)
41 CONTINUE
   WRITE (51,103) I
   WRITE (51,102) ET
50 RETURN
50 CALL PM(N,NH,NO,C,P,PA,C)
   IF(IPT(3)-3) 61,62,61
61 NO1 = NO-1
   GO TO 63
62 NO1 = NO
63 CALL PM(N,NH,NO1,C,PP,PB,0)
   DO 90 I = 1,NOC
   DO 68 J = 1,N
     PA(J) = 0.5*(PA(J)+PB(J))
     PB(J) = PA(J)
     CALL SETF(N,NH,P,PA,G,V,BETA,S,Z,F,U,IPT)
     IF(IPT(1)-1) 75,75,74
74 CALL INTER(N,NH,C,P,PA,F)
75 CALL HDIAG(F,C,U,NT,NR)
     IF(IPT(1)-1) 77,77,76
76 WRITE (51,101)
     WRITE (51,100) (F(J,J), J = 1,NT)
77 DO 70 J = 1,NT
     DO 70 K = 1,NT
       F(J,K) = P(J,K)
     CALL PM(N,NH,NO,C,P,PA,0)
     CALL COMPR(N,NH,F,P,KEY)
     IF(KEY) 80,95,80
80 CALL SETF(N,NH,PP,PB,G,V,BETA,S,Z,F,U,IPT)
     IF(IPT(1)-1) 85,85,84
84 CALL INTER(N,NH,C,PP,PB,F)
85 CALL HDIAG(F,C,U,NT,NR)
     IF(IPT(1)-1) 87,87,86
86 WRITE (51,101)
     WRITE (51,100) (F(J,J), J = 1,NT)

```

```

87 CALL PM(N,NH,NOL,C,PP,PB,U)
90 CONTINUE
95 DO 96 J = 1,NT
   DO 96 K = 1,NT
     F(J,K) = 0.5*(P(J,K)-PP(J,K))
96 P(J,K) = 0.5*(P(J,K)+PP(J,K))
   DO 120 J = 1,N
120 PA(J) = PB(J)
     WRITE (51,106)
   DO 97 J = 1,NT
     WRITE (51,100) (F(J,K), K = 1,NT)
     WRITE (51,108)
   DO 98 J = 1,NT
     WRITE (51,100) (P(J,K), K = 1,NT)
     WRITE (51,107)
     WRITE (51,100) (PA(J), J = 1,N)
   GO TO 35
100 FORMAT (1H,10F10.6)
101 FORMAT (17H ORBITAL ENERGIES)
102 FORMAT (1H,F14.8)
103 FORMAT (1H,13,11H ITERATIONS)
104 FORMAT (7H ENERGY)
105 FORMAT (24H NORMALIZED EIGENVECTORS)
106 FORMAT (20H SPIN DENSITY MATRIX)
107 FORMAT (3H PA)
108 FORMAT (2H P)
   END

SUBROUTINE INITL(N,NH,BETA,U,S,F)
DIMENSION BETA(40), U(40), S(40,40), F(40,40)
NT = 4*(N-NH)+NH
DO 10 I = 1,NT
10 F(I,I) = U(I)
DO 20 I = 1,NT
11 = I+1
DO 20 J = 1,NT

```

C

```

F(I,J) = 0.5*(BETA(I)+BETA(J))*S(I,J)
20 F(J,I) = F(I,J)
RETURN
END

```

C

```

SUBROUTINE PM(N,NH,NO,C,P,PA,IPT)
DIMENSION C(40,40), P(40,40), PA(18)
NT = 4*(N-NH)+NH
NOT = N-NH
DO 10 I = 1,NT
DO 10 J = 1,NT
P(I,J) = 0.0
DO 10 K = 1,NO
10 P(I,J) = P(I,J)+C(K,I)*C(K,J)
DO 20 I = 1,NT
DO 20 J = 1,NT
P(I,J) = 2.0*P(I,J)
IF(IPT) 21,25,21
21 DO 24 I = 1,NT
DO 24 J = 1,NT
24 P(I,J) = P(I,J) -C(NO,I)*C(NO,J)
25 DO 30 I = 1,NOT
ISUB = 4*I-3
ISUB4 = ISUB+3
PA(I) = 0.0
DO 30 J = ISUB,ISUB4
30 PA(I) = PA(I)+P(J,J)
NOT1 = NOT+1
DO 40 I = NOT1,N
ISUB = I+3*NOT
40 PA(I) = P(ISUB,ISUB)
RETURN
END

```

C

```

SUBROUTINE SETF(N,NH,P,PA,G,V,BETA,S,Z,F,U,IPT)
DIMENSION P(40,40), PA(18), G(18,18), V(18,18), BETA(40),

```



```

15(4,40), F(40,40), Z(18), U(40,40), IPT(5)
CALL INITL(N,NH,BETA,U,S,F)
NOT = N-NH
NS = 4*NOT
NT = NS+NH
FIPT = IPT(4)
DO 10 IM = 1,NT
IF(IM-NS) 5,5,6
5 IA = (IM+5)/4
GO TO 7
6 IA = IM-3*NOT
7 F(IM,IM) = F(IM,IM)-(Z(IA,IM)-1.0/FIPT)*G(IA,IA), (PA(IA)-0.5*P(IM,IM)
  1)*G(IA,IA)
DO 10 IB = 1,N
IF(IB-IA) 9,10,9
9 F(IM,IM) = F(IM,IM)+PA(IB)*G(IA,IB)-V(IA,IB)
10 CONTINUE
DO 40 IM = 1,NT
IM1 = IM+1
IF(IM-NS) 25,25,26
25 IA = (IM+3)/4
GO TO 27
26 IA = IM-3*NOT
27 DO 40 IN = IM1,NT
IF(IN-NS) 33,35,36
35 IB = (IN+5)/4
GO TO 37
36 IB = IN-3*NOT
37 F(IM,IN) = F(IM,IN)-0.5*P(IM,IN)*G(IA,IB)
40 CONTINUE
DO 50 I = 1,NT
I1 = I+1
DO 50 J = I1,NT
50 F(J,I) = F(I,J)
RETURN
END

```

```

SUBROUTINE COMPR(N,NH,P,U,G,BETA,S,Z,RAD,PA,E,ET,V,IPT)
DIMENSION C(40,40), P(40,40)
NT = 4*(N-NH)+NH
DO 10 I = 1,NT
DO 10 J = 1,NT
IF(ABSF(C(I,J)-P(I,J))-0.0001) 10,10,20
10 CONTINUE
KEY = 0
GO TO 30
20 KEY = 1
30 RETURN
END

```

```

SUBROUTINE ENRGY(N,NH,P,U,G,BETA,S,Z,RAD,PA,E,ET,V,IPT)
DIMENSION P(40,40), U(40), G(18,18), BETA(40), S(40,40), Z(18),
1RAD(18,18), PA(18), E(18,18), V(18,18), IPT(5)
NOT = N-NH
NM = N-1
FIPT = IPT(4)
DO 40 IA = 1,N
E(IA,IA) = 0.0
IF(IA-NOT) 15,15,16
15 IMN = 4*IA-3
IMX = IMN+3
GO TO 28
16 IMN = 3*NOT+IA
IMX = IMN
28 DO 40 IM = IMN,IMX
E(IA,IA) = E(IA,IA) + P(IM,IM)*(U(IM)-(Z(IA)-1.0/FIPT))*G(IA,IA))
DO 40 IN = IMN,IMX
40 E(IA,IA) = E(IA,IA)+0.5*(P(IM,IM)*P(IN,IN)
1 - .5*P(IM,IN)**2)*G(IA,IA)
DO 140 IA = 1,NM
IA1 = IA+1
IF(IA-NOT) 115,115,116

```

```

110 IMN = 4*IA-3
    IMX = IMN+3
    GO TO 118
110 IMN = 3*NOT+IA
    IMX = IMN
118 DO 140 IB = IA, N
    IF (IB-NOT) 125, 125, 126
125 INN = 4*IB-3
    INX = INN+3
    GO TO 128
126 INN = 3*NOT+IB
    INX = INN
120 L(IA,IB) = Z(IA)*Z(IB)/RAD(IA,IB) PA(IA)*V(IA,IB)
    1 - PA(IB)*V(IB,IA) + PA(IA)*PA(IB)*G(IA,IB)
    DO 140 IM = IMN, IMX
    DO 140 IN = INN, INX
140 E(IA,IB) = E(IA,IB) + P(IM,IN)*(BETA(IM)+BETA(IN))*S(IM,IN)
    1 - .5*P(IM,IN)**2*G(IA,IB)
    DO 141 I = 1, N
    I1 = I+1
    DO 141 J = I1, N
141 E(J,I) = 0.0
    ET = 0.0
    DO 80 I = 1, N
    DO 80 J = 1, N
    80 ET = ET+E(I,J)
    RETURN
    END
C
SUBROUTINE FRST(N,NH,COORD,COS,RAD,RHO,TAU,S,F,G,V)
DIMENSION COORD(3,18), COS(3,18,18), RAD(18,18), RHO(18,18),
1TAU(18,18), S(40,40), F(40,40), G(18,18), V(18,18)
NT = 4*(N-NH)+NH
WRITE (51,100)
DO 10 I = 1, N
10 WRITE (51,120) (COORD(J,I), J = 1,3)

```

```

WRITE (51,101)
DO 20 I = 1,3
DO 20 J = 1,N
20 WRITE (51,120) (COS(I,J,K), K = 1,N)
WRITE (51,102)
DO 25 I = 1,N
25 WRITE (51,120) (RAD(I,J), J = 1,N)
WRITE (51,103)
DO 26 I = 1,N
26 WRITE (51,120) (RHO(I,J), J = 1,N)
WRITE (51,104)
DO 27 I = 1,N
27 WRITE (51,120) (TAU(I,J), J = 1,N)
WRITE (51,105)
DO 30 I = 1,NT
30 WRITE (51,120) (S(I,J), J = 1,NT)
WRITE (51,106)
DO 35 I = 1,N
35 WRITE (51,120) (G(I,J), J = 1,N)
WRITE (51,107)
DO 40 I = 1,N
40 WRITE (51,120) (V(I,J), J = 1,N)
WRITE (51,108)
DO 45 I = 1,NT
45 WRITE (51,120) (F(I,J), J = 1,NT)
RETURN
100 FORMAT (28H COORDINATES IN ATOMIC UNITS)
101 FORMAT (18H DIRECTION COSINES)
102 FORMAT (26H DISTANCES IN ATOMIC UNITS)
103 FORMAT (4H RHO)
104 FORMAT (4H TAU)
105 FORMAT (8H OVERLAP)
106 FORMAT (6H GAMMA)
107 FORMAT (2H V)
108 FORMAT (2H F)
120 FORMAT (1H ,10F11.6)

```



```

C
END

SUBROUTINE INTER(N,NH,C,P,PA,F)
DIMENSION C(40,40), P(40,40), PA(18), F(40,40)
WRITE (51,100)
NT = (N-NH)*4+NH
DO 10 I = 1,NT
10 WRITE (51,120) (C(I,J), J = 1,NT)
   WRITE (51,101)
DO 20 I = 1,NT
20 WRITE (51,120) (P(I,J), J = 1,NT)
   WRITE (51,102)
   WRITE (51,120) (PA(I), I = 1,N)
   WRITE (51,103)
DO 30 I = 1,NT
30 WRITE (51,120) (F(I,J), J = 1,NT)
   RETURN
100 FORMAT (2H C)
101 FORMAT (2H P)
102 FORMAT (3H PA)
103 FORMAT (2H F)
120 FORMAT (1H ,10F11.6)
END

```

```

C
SUBROUTINE PREL(N,COORD,COS,RAD,ZS,RHO,TAU,NH)
DIMENSION COORD(3,18), COS(3,18,18), RAD(18,18)
12S(18), RHO(18,18), TAU(18,18)
DO 5 I = 1,3
DO 5 J = 1,N
5 COORD(I,J) = COORD(I,J)/.529167
DO 10 I = 1,N
DO 10 J = 1,N
RAD(I,J) = SQRT((COORD(1,J)-COORD(1,I))**2
1 + (COORD(2,J)-COORD(2,I))**2 + (COORD(3,J)-COORD(3,I))**2)
DO 10 K = 1,3
10 COS(K,I,J) = (COORD(K,J)-COORD(K,I))/RAD(I,J)

```

```

DO 30 I = 1,N
DO 30 J = 1,N
RHU(I,J) = 0.5*(ZS(I)+ZS(J))*RAD(I,J)
30 TAU(I,J) = (ZS(I)-ZS(J))/(ZS(I)+ZS(J))
RETURN
END

C
SUBROUTINE OVERL(N,NH,ZS,COORD,COS,RAD,S,RHO,TAU)
DIMENSION ZS(18), COORD(3,18), COS(3,18,18), RAD(18,18), S(40,40),
1CA(3,3), CB(3,3), CC(3,3), RHO(18,18), TAU(18,18)
C THIS ROUTINE CALCULATES THE OVERLAP MATRIX S, GIVEN
C N, THE NUMBER OF ATOMS
C NH, THE NUMBER OF HYDROGEN ATOMS
C ZS, THE ARRAY OF SLATER EXPONENTS
C COORD, THE MATRIX OF CARTESIAN COORDINATES, IN ATOMIC UNITS
C COS, THE DIRECTION COSINE MATRIX
C RAD, THE DISTANCE MATRIX, IN ATOMIC UNITS
C RHO,
C AND TAU.
C THIS ROUTINE MAKES USE OF SUBROUTINES
SF(KEY,P,I) WHICH ALSO USES FUNCTION ABF
C THE S MATRIX IS SET UP IN THE BASIS WHICH INCLUDES THE ROW TWO
C ELEMENTS FIRST, THEN THE HYDROGEN ATOMS. EACH ROW TWO ELEMENT
C IS ARRANGED SEPARATELY, WITH THE BASIS ARRANGED S, PX, PY, PZ FOR EACH.
NOT = N-NH
NOT1 = NOT+1
NS = 4*NOT
NS1 = NS+1
NT = NS+NH
DO 5 I = 1,NT
DO 5 J = 1,NT
5 S(I,J) = 0.0
DO 6 I = 1,NT
6 S(I,I) = 1.0

C
C CALCULATE PERIOD 2 ATOM OVERLAP INTEGRALS

```

```

DO 20 I = 1,NOT
  I1 = I+1
  DO 20 J = I1,NOT
    ISUB = 4*I-3
    JSUB = 4*J-3
    P = RHO(I,J)
    T = TAU(I,J)
    S(ISUB,JSUB) = SF(4,P,T)
    TA = SF(5,P,T)
    TB = SF(5,P,-T)
    DO 12 K = 1,3
      JK = JSUB+K
      S(ISUB,JK) = TA*CS(K,J,I)
      IK = ISUB+K
12  S(IK,JSUB) = TB*CS(K,I,J)
    DO 14 K = 1,3
      DO 14 L = 1,3
        CA(K,L) = 0.0
        CB(K,L) = 0.0
        CC(K,L) = 0.0
14  CB(1,1) = SF(6,P,T)
      CB(2,2) = SF(7,P,T)
      CB(3,3) = CB(2,2)
      DEN = SQRTF(COS(2,I,J)**2+COS(3,I,J)**2)
      CA(1,1) = COS(1,I,J)
      IF(DEN-.000001) 16,16,18
16  CA(2,2) = 1.0
      CA(3,3) = 1.0
      GO TO 19
18  CA(1,2) = COS(2,I,J)
      CA(1,3) = COS(3,I,J)
      CA(2,2) = COS(3,I,J)/DEN
      CA(2,3) = -COS(2,I,J)/DEN
      CA(3,1) = -(CA(1,2)**2+CA(1,3)**2)/DEN
      CA(3,2) = CA(1,1)*CA(1,2)/DEN

```

```

      CA(3,3) = CA(1,1)*CA(1,3)/DEN
19 DO 15 K = 1,3
   DO 15 L = 1,3
15 CC(K,L) = CA(K,L)
   DO 17 K = 1,3
   DO 17 L = 1,3
      IK = ISUB+K
      IL = JSUB+L
      S(IK,IL) = 0.0
   DO 17 M = 1,3
17 S(IK,IL) = S(IK,IL)+CA(M,K)*CB(M,M)*CC(M,L)
20 CONTINUE

C
C CALCULATE PERIOD 2 - HYDROGEN OVERLAP INTEGRALS
C
      DO 40 I = 1,NOT
      I1 = 4*I-3
      I2 = I1+1
      I3 = I2+1
      I4 = I3+1
      DO 40 J = NOT1,N
      JSUB = 3*NOT+J
      P = RHO(I,J)
      T = TAU(I,J)
      S(I1,JSUB) = SF(2,P,T)
      SFS = SF(3,P,T)
      S(I2,JSUB) = SFS*COS(1,I,J)
      S(I3,JSUB) = SFS*COS(2,I,J)
      S(I4,JSUB) = SFS*COS(3,I,J)
40 S(I4,JSUB) = SFS*COS(3,I,J)

C
C CALCULATE HYDROGEN OVERLAP INTEGRALS
C
      NB = 3*NOT
      DO 60 I = NOT1,N
      I1 = I+1
      ISUB = NB+I

```



```

DO 60 J = I1,N
JSUB = NB+J
60 S(JSUB,JSUB) = SF(1,RHO(I,J),TAU(I,J))
DO 80 I = 1,NT
I1 = I+1
DO 80 J = I1,NT
80 S(J,I) = S(I,J)
RETURN
END

C
FUNCTION SF(KEY,P,T)
TS = ABSF(T)
IF(ABSF(T)-0.000001) 2,2,1
1 GO TO (10,20,30,40,50,60,70) KEY
2 GO TO (110,120,130,140,150,160,170) KEY
1S1S, 1S2S, 1S2PS, 2S2S, 2S2PS, 2PS2PS, 2PP2PP
10 SF = (P**3/4.0)*SQRTF((1.0-T**3)*(ABF(1,2,P,TS)*ABF(2,0,P,TS) -
1 ABF(1,0,P,TS)*ABF(2,2,P,TS))
RETURN
20 SF = (P**4/8.0)*SQRTF((1.0+T)**3*(1.0-T)**5/3.0)*(ABF(1,3,P,T)*
1ABF(2,0,P,T) - ABF(1,2,P,T)*ABF(2,1,P,T) - ABF(1,1,P,T)*ABF(2,2,P,
2T) + ABF(1,0,P,T)*ABF(2,3,P,T))
RETURN
30 SF = (P**4*SQRTF((1.0+T)**3*(1.0-T)**5/8.0)*(-ABF(1,3,P,T)*ABF(
1 2,1,P,T) + ABF(1,2,P,T)*ABF(2,0,P,T) + ABF(1,1,P,T)*ABF(2,3,P,T)
2 - ABF(1,0,P,T)*ABF(2,2,P,T))
RETURN
40 SF = (P**5*SQRTF((1.0-T**5)/48. ) * (ABF(1,4,P,TS)*ABF(2,0,P,TS
1) - 2.0*ABF(1,2,P,TS)*ABF(2,2,P,TS) + ABF(1,0,P,TS)*ABF(2,4,P,TS))
RETURN
50 SF = (P**5*SQRTF((1.0-T**2)**5/3.0)/16.0)*
1(ABF(1,3,P,T)*(ABF(2,0,P,T)-ABF(2,2,P,T)) +
2ABF(1,1,P,T)*(ABF(2,4,P,T)-ABF(2,2,P,T)) +
3ABF(2,1,P,T)*(ABF(1,2,P,T)-ABF(1,4,P,T)) +
4ABF(2,3,P,T)*(ABF(1,2,P,T)-ABF(1,0,P,T)))
RETURN

```

```

60 SF = (P**5/16.0)*SQRTF((1.0-T*T)**5) *
1  (ABF(2,2,P,TS)*(ABF(1,0,P,TS) + ABF(1,4,P,TS)) -
2  ABF(1,2,P,TS)*(ABF(2,0,P,TS) + ABF(2,4,P,TS)))
RETURN
70 SF = (P**5/32.0) * SQRTF((1.0-T*T)**5) *
1  (ABF(1,4,P,TS)*(ABF(2,0,P,TS)-ABF(2,2,P,TS)) +
2  ABF(1,2,P,TS)*(ABF(2,4,P,TS)-ABF(2,0,P,TS)) +
3  ABF(1,0,P,TS)*(ABF(2,2,P,TS)-ABF(2,4,P,TS)))
RETURN
110 SF = (P**3/6.0)*(3.0*ABF(1,2,P,T)-ABF(1,0,P,T))
RETURN
120 SF = (P**4/(12.0*SQRTF(3.0)))*(3.0*ABF(1,3,P,T)-ABF(1,1,P,T))
RETURN
130 SF = (P**4/12.0)*(3.0*ABF(1,2,P,T) ABF(1,0,P,T))
RETURN
140 SF = (P**5/360.0)*(15.0*ABF(1,4,P,T)-10.0*ABF(1,2,P,T)+3.0*ABF(1,0
1,P,T))
RETURN
150 SF = (P**5/(60.0*SQRTF(3.0)))*(5.0*ABF(1,3,P,T)-ABF(1,1,P,T))
RETURN
160 SF = (P**5/120.0)*(5.0*ABF(1,4,P,T)-18.0*ABF(1,2,P,T) +
15.0*ABF(1,0,P,T))
RETURN
170 SF = (P**5/120.0)*(5.0*ABF(1,4,P,T)-6.0*ABF(1,2,P,T) +
1ABF(1,0,P,T))
RETURN
END

FUNCTION ABF(KAB,KP,P,T)
DIMENSION FACT(10), DUM(2)
EQUIVALENCE (DUM(2),FACT(1))
KP1 = KP+1
IF(IFBF-12345) 10,20,10
10 DUM(2) = 1.0
DO 12 I = 1,10
FI = I

```

C

```

12 FACT(I) = FACT(I-1)*FI
   IFBF = 12345
20 ABF = 0.0
   GO TO (30,130) KAB
30 DO 40 M = 1,KP1
   KM1 = KP-M+1
40 ABF = ABF+1.0/(P**M*FACT(KM1))
   ABF = ABF*FACT(KP)*EXP(-P)
   RETURN
130 BA = 0.0
   BB = 0.0
   PT = P*T
   DO 140 M = 1,KP1
   KM = KP-M
   KM1 = KP-M+1
   ABF = 1.0/((P*T)**M*FACT(KM1))
   BA = BA+ABF
140 BB = BB+(-1.0)**KM*ABF
   EPT = EXP(-PT)
   ABF = -EPT*FACT(KP)*BA-FACT(KP)*BB/EPT
   RETURN
   END

C
SUBROUTINE GVAB(N,NH,ZS,RAD,G,V,RHO,TAU,Z,IPT)
DIMENSION ZS(18), RAD(18,18), G(18,18), V(18,18), RHO(18,18),
1TAU(18,18), IPT(5), Z(18)
   NOT = N-NH
   NOT1 = NOT+1
   DO 10 I = 1,N
   DO 10 J = 1,N
   G(I,J) = 0.0
10 V(I,J) = 0.0
   DO 20 I = 1,NOT
   I1 = I+1
   DO 20 J = I1,NOT
   G(I,J) = GF(3,RHO(I,J),TAU(I,J),RAD(I,J))

```

```

G(J,I) = G(I,J)
RD = RAD(I,J)
P = ZS(I)*RD
V(I,J) = VF(2,P,RD)*Z(J)
P = ZS(J)*RD
20 V(J,I) = VF(2,P,RD) *Z(I)
DO 40 I = 1,NOT
DO 40 J = NOT1,N
RD = RAD(I,J)
G(I,J) = GF(2,RHO(I,J),-TAU(I,J),RD)
G(J,I) = G(I,J)
P = ZS(I)*RD
V(I,J) = VF(2,P,RD)*Z(J)
P = ZS(J)*RD
40 V(J,I) = VF(1,P,RD)*Z(I)
DO 60 I = NOT1,N
I1 = I+1
DO 60 J = I1,N
G(I,J) = GF(1,RHO(I,J),TAU(I,J),RAD(I,J))
G(J,I) = G(I,J)
RD = RAD(I,J)
P = ZS(I)*RD
V(I,J) = VF(1,P,RD)*Z(J)
P = ZS(J)*RD
60 V(J,I) = VF(1,P,RD)*Z(I)
DO 80 I = 1,NOT
80 G(I,I) = 0.36328125*ZS(I)
DO 81 I = NOT1,N
81 G(I,I) = 0.625*ZS(I)
IF(IPT(4)-2) 90,85,90
85 DO 87 I = 1,N
DO 87 J = 1,N
87 V(I,J) = Z(J)*G(I,J)
DO 88 I = 1,N
88 V(I,I) = 0.0
90 RETURN

```



```

C
END
FUNCTION GF(KEY,P,T,R)
IF(ABSF(T)-0.000001) 1,1,2
1 GO TO (110,120,130) KEY
2 AK = 0.5*(T+1.0/T)
PA = (1.0+T)*P
PB = (1.0-T)*P
GO TO (10,20,30) KEY
10 GF = (1.0-(1.0-AK)**2*((2.0+AK)/4. PA/4.0)*EXPF(-2.0*PA) -
1 (1.0+AK)**2*((2.0-AK)/4.0+PB/4.0)*EXPF(-2.0*PB))/R
GO TO 100
20 GF = (1.0-(1.0-AK)**3*((1.0-5.0*AK 4.0*AK**2)/16.0-AK*PA/8.0)*
1 EXPF(-2.0*PA) - (1.0+AK)**2*((15.0 22.0*AK+15.0*AK**2-4.0*AK**3)
2 /16.0+3.0*(3.0-3.0*AK+AK**2)*PB/8. (2.0-AK)*PB**2/4.0+PB**3/12.0)*
3 EXPF(-2.0*PB))/R
GO TO 100
30 GF = (1.0-(1.0-AK)**3*((8.-AK-27.0*AK**2-30.0*AK**3-10.0*AK**4)/
1 16.0+(11.0-19.0*AK-44.0*AK**2-20. AK**3)*PA/32.0+(1.0-5.0*AK
2 -4.0*AK**2)*PA**2/16.0-AK*PA**3/24.0)*EXPF(-2.0*PA) - (1.0+AK)**3
3 *((8.+AK-27.0*AK**2+30.0*AK**3-10. AK**4)/16.0+(11.0+19.0*AK-44.0
4 *AK**2+20.0*AK**3)*PB/32.0+(1.0+5. AK-4.0*AK**2)*PB**2/16.0
5 +AK*PB**3/24.0)*EXPF(-2.0*PB))/R
GO TO 100
110 GF = (1.0-(1.0+11.0*P/8.0+3.0*P**2/4.0+P**3/6.0)*EXPF(-2.0*P))/R
GO TO 100
120 GF = (1.0-(1.0+25.0*P/16.0+9.0*P**2/8.0+23.0*P**3/48.0+P**4/8.0
1 +P**5/60.0)*EXPF(-2.0*P))/R
GO TO 100
130 GF = (1.0-(1.0+419.0*P/256.0+163.0*P**2/128.0+119.0*P**3/192.0
1 +5. *P**4/24.0+P**5/20.0+P**6/120. P**7/1260.0)*EXPF(-2.0*P))/R
100 RETURN
END
C
FUNCTION VF(KEY,P,R)
GO TO (10,20) KEY

```

```

10 VF = (1.0-(1.0+P) *EXPF(-2.0*P))/R
GO TO 100
20 VF = (1.0-(1.0+1.5*P+P**2+P**3/3.0)*EXPF(-2.0*P))/R
100 RETURN
END

```

C

```

SUBROUTINE HDIAG(H,U,IEGEN,N,NR)
DIMENSION H(40,40), ROOT(40), U(40,40), B(40,5)
IC = 0
DO 10 J = 1,N
DO 10 I = 1,J
IC = IC+1
10 H(IC) = H(I,J)
CALL GIVENS(N,N,H,B,ROOT,U)
IC = 0
DO 30 I = 1,N
DO 30 J = 1,N
IC = IC+1
30 H(J,I) = U(IC)
DO 40 I = 1,N
DO 40 J = 1,N
U(I,J) = H(J,I)
40 H(J,I) = 0.0
DO 50 I = 1,N
50 H(I,I) = ROOT(I)
RETURN
END

```

SUBROUTINE GIVENS (NX,NROOTX,A,B,ROOT,VECT)

EIGENVALUES AND EIGENVECTORS BY GIVENS METHOD.

CALCULATES EIGENVALUES AND EIGENVECTORS OF REAL SYMMETRIC MATRIX
BY THE MODIFIED GIVENS METHOD. THE PARAMETERS ARE...

NX ORDER OF MATRIX

0003
4
5
0006
7
8
0009
000
0010

C	NROOTX	NUMBER OF ROOTS WANTED. MOST NEGATIVE ROOTS ARE	0011
C		FOUND FIRST. IF NO VECTORS ARE WANTED, MAKE THIS	0012
C		NUMBER NEGATIVE.	0013
C	A	MATRIX STORED BY COLUMNS IN PACKED UPPER TRIANGULAR	0014
C		FORM, I.E. OCCUPYING $NX*(NX+1)/2$ CONSECUTIVE	0015
C		LOCATIONS.	0016
C	ROOT	ARRAY TO HOLD THE EIGENVALUES. MUST BE AT LEAST	0017
C		NROOTX CELLS LONG.	0018
C	VECT	EIGENVECTOR ARRAY. EACH COLUMN WILL HOLD AN	0019
C		EIGENVECTOR FOR THE CORRESPONDING ROOT. MUST BE	0020
C		AT LEAST $NX*NROOTX$ CELLS LONG, UNLESS NO VECTORS	0021
C		ARE REQUESTED (NEGATIVE NROOTX). IN THIS LATTER	0022
C		CASE, THE ARGUMENT VECT IS JUST A DUMMY, AND THE	0023
C		STORAGE IS NOT USED.	0024
			25
C		THE ARRAYS A AND B ARE DESTROYED BY THE COMPUTATION. THE RESULTS	0026
C		APPEAR IN ROOT AND VECT.	0027
			28
C		THE ORIGINAL REFERENCE TO THE GIVENS TECHNIQUE IS IN OAK RIDGE	0029
C		REPORT NUMBER ORNL 1574 (PHYSICS), BY WALLACE GIVENS.	0030
C		THE METHOD AS PRESENTED IN THIS PROGRAM CONSISTS OF FOUR STEPS,	0031
C		ALL MODIFICATIONS OF THE ORIGINAL METHOD...	0032
C		FIRST, THE INPUT MATRIX IS REDUCED TO TRIDIAGONAL FORM BY THE	0033
C		HOUSEHOLDER TECHNIQUE (J. H. WILKINSON, COMP. J. 3, 23 (1960)).	0034
C		THE ROOTS ARE THEN LOCATED BY THE STURM SEQUENCE METHOD (J. M.	0035
C		ORTEGA, J.ACM 7, 260 (1960)). THE VECTORS OF THE TRIDIAGONAL	0036
C		FORM ARE THEN EVALUATED (J. H. WILKINSON, COMP. J. 1, 90 (1958)),	0037
C		AND LAST THE TRIDIAGONAL VECTORS ARE ROTATED TO VECTORS OF THE	0038
C		ORIGINAL ARRAY (FIRST REFERENCE).	0039
			40
C		VECTORS FOR DEGENERATE (OR NEAR-DEGENERATE) ROOTS ARE FORCED	0041
C		TO BE ORTHOGONAL, USING A METHOD SUGGESTED BY B. GARBOW, ARGONNE	0042
C		NATIONAL LABS (PRIVATE COMMUNICATION, 1964). THE GRAM-SCHMIDT	0043
C		PROCESS IS USED FOR THE ORTHOGONALIZATION.	0044
			45
			46

```

0047 DIMENSION B(NX,5), A(1), ROOT(1), VECT(NX,NROOTX)
0048 DATA (KILLBIT = 7777777777777776B),(ETA = 1.0E-10)
    49
0050 N = NX
0051 NROOT = XABSF(NROOTX)
0052 GO TO (1010,105) N
0053 ROOT = A
0054 GO TO 807
0055 CONTINUE
    56
0057 C      NSIZE  NUMBER OF ELEMENTS IN THE ARRAY
0058 NSIZE = N*(N+1)/2
0059 NM1 = N - 1
0060 NM2 = N - 2
    61
0062 C      TRIDIAGONALIZATION OF SYMMETRIC MATRIX
    63
    64
    65 ID = 0
    66 IA = 1
    67
    68 DO 200 J=1,NM2
    69 J      COUNTS ROWS OF A-MATRIX TO BE DIAGONALIZED
    70 IA     START OF NON-CODIAGONAL ELEMENTS IN THE ROW
    71 ID     POSITION OF DIAGONAL ELEMENT ON ROW BEING CODIAGONALIZED
    72 IA = IA+J+2
    73 ID = ID + J
    74 JUMP = J+1
    75
    76 C      SUM SQUARES OF NON-CODIAGONAL ELEMENTS IN ROW J
    77 SUM = 0.0
    78 DO 100 I=IA,NSIZE,JUMP
    79 SUM = SUM + A(I)**2
    80 JUMP = JUMP + 1
    81 TEMP = A(ID+J)
    82 IF(SUM) 110,120,110
    83
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C	NO TRANSFORMATION NECESSARY IF ALL THE NON-CODIAGONAL	83
C	ELEMENTS ARE ZERO.	0084
120	B(J) = TEMP	0085
	A(ID+J) = 0.0	0086
	GO TO 200	0087
		0088
		89
C	NOW COMPLETE THE SUM OF OFF-DIAGONAL SQUARES	0090
110	SUM = SQRTF(SUM+ TEMP**2)	0091
		92
C	NEW CODIAGONAL ELEMENT	0093
	B(J) = -SIGNF(SUM,TEMP)	0094
		95
C	FIRST NON-ZERO ELEMENT OF THIS W-VECTOR	0096
	JUMP = J + 1	0097
	B(JUMP,2) = SQRTF((1.0 + ABSF(TEMP)/SUM)/2.0)	0098
		99
C	FORM REST OF THE W-VECTOR ELEMENTS	0100
	TEMP = SIGNF(0.5/(B(JUMP,2)*SUM),TEMP)	0101
	DO 130 I=IA,NSIZE,JUMP	0102
	JUMP = JUMP + 1	0103
130	B(JUMP,2) = A(I)*TEMP	0104
		105
C	FORM P-VECTOR AND SCALAR. P-VECTOR = A-MATRIX*W-VECTOR.	0106
C	SCALAR = W-VECTOR*P-VECTOR.	0107
		108
	AK = 0.0	0109
C	IC LOCATION OF NEXT DIAGONAL ELEMENT	0110
	IC = ID + J + 1	0111
	J1 = J + 1	0112
		113
	DO 190 I=J1,N	0114
	JJ = IC	0115
	TEMP = 0.	0116
	DO 180 II=J1,N	0117
		118

C	I	RUNS OVER THE NON-ZERO P-ELEMENTS	0119
C	II	RUNS OVER ELEMENTS OF W-VECTOR	0120
	TEMP = TEMP + B(II,2)*A(JJ)		0121
			122
			0123
C	CHANGE INCREMENTING MODE AT THE DIAGONAL ELEMENTS		
	IF(II-I) 210,140,140		0125
140	JJ = JJ + II		0126
	GO TO 180		0127
210	JJ = JJ + 1		0128
180	CONTINUE		129
C	BUILD UP THE K-SCALAR (AK)		0130
	AK = AK + TEMP*B(I,2)		0131
	B(I) = TEMP		0132
C	MOVE IC TO TOP OF NEXT A-MATRIX -ROW-		0133
190	IC = IC + I		0134
			135
C	FORM THE Q-VECTOR		0136
	DO 150 I=J1,N		0137
150	B(I) = B(I) - AK*B(I,2)		0138
			139
C	TRANSFORM THE REST OF THE A-MATRIX		0140
C	JJ START-1 OF THE REST OF THE A-MATRIX		0141
	JJ = ID + J		0142
C	MOVE W-VECTOR INTO THE OLD A-MATRIX LOCATIONS TO SAVE SPACE		0143
C	I RUNS OVER THE SIGNIFICANT ELEMENTS OF THE W-VECTOR		0144
	DO 160 I=J1,N		0145
	A(JJ) = B(I,2)		0146
			147
	DO 170 II=J1,I		0148
	JJ = JJ + 1		0149
170	A(JJ) = A(JJ) - 2.0*(B(I)*B(II,2) B(I,2)*B(II))		0150
160	JJ = JJ + J		0151
200	CONTINUE		0152
C	MOVE LAST CODIAGONAL ELEMENT OUT INTO ITS PROPER PLACE		153
			0154

```

C      B(N-1) = A(NSIZE-1)
C      A(NSIZE-1) = 0.0
C
C      SHIFT ALL CODIAGONAL ELEMENTS DOWN ONE PLACE TO TAKE ADVANTAGE
C      OF FORWARD INDEXING (I.E. FIRST CODIAGONAL ELEMENT MUST BE ZERO).
C      DO 205 J=1,NM1
C      B(N+1-J) = B(N-J)
C      B(1) = 0.
205
C
C      STURM SEQUENCE ITERATION TO OBTAIN ROOTS OF TRIDIAGONAL FORM
C      - - - - -
C
C      MOVE DIAGONAL ELEMENTS INTO SECOND N ELEMENTS OF B-VECTOR.
C      THIS IS A MORE CONVENIENT INDEXING POSITION.
C      ALSO, PUT SQUARE OF CODIAGONAL ELEMENTS IN THIRD N ELEMENTS
C      OF B-VECTOR FOR USE IN STURM SEQUENCE EVALUATION.
C      AT THE SAME TIME, COMPUTE THE NORM OF THE MATRIX.
C
C      ANORM = 0.
C      JUMP = 1
C      DO 300 J=1,N
C      B(J,3) = B(J)**2
C      B(J,2) = A(JUMP)
C      ANORM = ANORM + 2.0*B(J,3) + A(JUMP)**2
C      JUMP = JUMP + J + 1
300
C
C      NORM OF MATRIX AND SMALL CONVERGENCE LIMIT.
C      ANORM = SQRTF(ANORM)
C      DELTA = ANORM*ETA
C      IF (DELTA) 320,1001
C      ROOT(1) HOLDS LOWER LIMIT OF EIGENVALUE I.
C      B(I,4) HOLDS UPPER LIMIT OF EIGENVALUE I.
320
C      DO 310 I=1,NROOT

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310	ROOT(I) = -ANORM	0191
C	B(I,4) = +ANORM	0192
	ISOLATE THE ROOTS.	0193
C	DO 330 I=1,NROOT	0194
500	IMPROVE THE TRIAL ROOT	0195
	TRIAL = (ROOT(I)+B(I,4))*0.5	0196
	IF((B(I,4)-ROOT(I))-DELTA) 330,330,350	
C	FORM STURM SEQUENCE.	198
C	NOMATCH IS ONE GREATER THAN THE NUMBER OF ROOTS LESS THAN	0199
C	THE TRIAL VALUE.	0200
350	NOMATCH = 1	0201
	F1 = 1.0	0202
	DO 360 J=1,N	0203
	DIAG = B(J,2) - TRIAL	0204
		0205
		206
420	IF (B(J)) 410,420	0207
	F0 = DIAG*SIGNF(1.0,F1)	0208
	GO TO 400	0209
410	F0 = DIAG*F1	210
	IF (B(J-1)) 430,440	0211
440	F0 = F0 - B(J,3)*SIGNF(1.0,F2)	0212
	GO TO 400	0213
		0214
430	F0 = F0 - B(J,3)*F2	215
		0216
400	IF (F0) 450,460,470	217
460	F0 = SIGNF(0.0,F1)	0218
	GO TO 510	0219
		0220
		221
480	IF(F0*SIGNF(1.0,F1)) 520,520,510	
470	IF (F1) 520,480,510	0223
450	IF (F1) 510,480,520	224
520	NOMATCH = NOMATCH + 1	0225
		0226

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510      F2 = F1
      F1 = F0
360      CONTINUE

C      ESTABLISH NEW BOUNDS FOR REMAINING ROOTS.
      DO 540 J=I,NROOT
      IF(J-NOMATCH) 600,610,610

C      NEW UPPER BOUND FOR THIS ROOT
600      B(J,4) = TRIAL
      GO TO 540

C      NEW LOWER BOUND FOR THIS ROOT
610      IF(ROOT(J)-TRIAL) 539,500,500
539      ROOT(J) = TRIAL
540      CONTINUE
      GO TO 500

330      CONTINUE

C      EIGENVECTORS OF CODIAGONAL FORM
C      - - - - -
807      CONTINUE

C      QUIT NOW IF NO VECTORS WERE REQUESTED.
      IF(NROOTX) 1002,808,808
808      NRSIZE = N*NROOT

C      SET INITIAL VALUES TO VECTORS TO TRY TO SOLVE THE
C      DEGENERACY PROBLEM FOR MOST CASES.
      VECT(1) = 1.0
      GO TO (1002,806) N
806      DO 805 I=2,NRSIZE

```



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805      VECT(I) = VECT(I-1) + 0.013125901
C      DON-T GET EXCITED. THE CONSTANT IS JUST A FACTOR TO TRY TO
C      DESTROY CYCLES IN THE STARTING VECTORS. THIS HELPS OUT THE
C      ALGORITHM IN SOME CASES WITH MANY DEGENERACIES.
                                0262
                                0263
                                0264
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                                0268
                                269
                                0270
                                0271
C      TEST FOR REPEATED ROOT (WITHIN A LIMIT OF DELTA)
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                                0289
                                0290
                                0291
                                292
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                                0294
                                295
                                0296
C      GO TO (710,715) I
                                0270
                                0271
C      IF((AROOT-ROOT(I-1))-DELTA) 720,71 ,710
                                0270
                                0271
C      IA = -1
                                0270
                                0271
C      IA = IA + 1
                                0270
                                0271
C      ELIM1 = A(1) - AROOT
                                0270
                                0271
C      ELIM2 = B(2)
                                0270
                                0271
C      JUMP = 1
                                0270
                                0271
C      DO 750 J=1,NM1
                                0270
                                0271
C      JUMP = JUMP+J+1
                                0270
                                0271
C      GET THE CORRECT PIVOT EQUATION FOR THIS STEP
                                0270
                                0271
C      IF(ABS(ELIM1)-ABS(B(J+1))) 760,755,755
                                0270
                                0271
C      FIRST (ELIM) EQUATION IS THE PIVOT THIS TIME
                                0270
                                0271
C      IF(ELIM1) 757,756,757
                                0270
                                0271
C      ELIM1 = DELTA
                                0270
                                0271
C      B(J,2) = ELIM1
                                0270
                                0271
C      B(J,3) = ELIM2
                                0270
                                0271
C      B(J,4) = 0.
                                0270
                                0271
C      TEMP = B(J+1)/ELIM1
                                0270
                                0271
C      SAVE FACTOR FOR THE SECOND ITERATION. MARK IT AS CASE 1
                                0270
                                0271
C      B(J,5) = TEMP.AND.KILLBIT
                                0270
                                0271
C      ELIM1 = A(JUMP)-AROOT - TEMP*ELIM2
                                0270
                                0271

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      ELIM2 = B(J+2)
      GO TO 750
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      C
      SECOND EQUATION IS THE PIVOT THIS TIME.
760  B(J,2) = B(J+1)
      B(J,3) = A(JUMP) - AROOT
      B(J,4) = B(J+2)
      TEMP = ELIM1/B(J+1)
0315
0316
317
0318
319

      C
      SAVE FACTOR FOR SECOND ITERATION.  MARK IT AS CASE 2
      B(J,5) = TEMP.OR.1B
321
0322
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0331

      IF(ELIM1) 752,751,752
751  ELIM1 = DELTA
752  B(N,2) = ELIM1
      B(N,3) = B(N,4) = 0.
      B(N-1,4) = 0.
      ITER = 1
0315
0316
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319

      IF(IA) 800,790,800
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      C
      BACK SUBSTITUTE TO GET THIS VECTOR
790  L = N + 1
      DO 780 J=1,N
      L = L - 1
780  VECT(L,I) =(VECT(L,I) - VECT(L+1,I)*B(L,3) - VECT(L+2,I))*
      X      B(L,4))/B(L,2)
      GO TO (820,800) ITER

      C
      SECOND ITERATION.  (BOTH ITERATIONS FOR REPEATED-ROOT VECTORS)
820  ITER = ITER + 1

```

890	ELIM1 = VECT(1,I)	0332
	DO 830 J=1,NM1	0333
	TEMP = B(J,5).AND.1B	0334
	IF (TEMP) 840,850	0335
		336
C	CASE ONE.	0337
850	VECT(J,I) = ELIM1	0338
	ELIM1 = VECT(J+1,I) - ELIM1*B(J,5)	0339
	GO TO 830	0340
		341
C	CASE TWO.	0342
840	VECT(J,I) = VECT(J+1,I)	0343
	TEMP = B(J,5).AND.KILLBIT	0344
	ELIM1 = ELIM1 - VECT(J+1,I)*TEMP	0345
		346
830	CONTINUE	0347
	VECT(N,I) = ELIM1	0348
	GO TO 790	0349
		350
C	ORTHOGONALIZE THIS REPEATED-ROOT VECTOR TO OTHERS WITH THIS ROOT	0351
C	IF THIS SECTION IS ENTERED WITH IA=0, THE SECTION IS A NO-OP.	0352
800	DO 860 J1=1,IA	0353
	K = I - J1	0354
	TEMP = 0.	0355
		356
870	DO 870 J=1,N	0357
	TEMP = TEMP + VECT(J,I)*VECT(J,K)	0358
		359
880	DO 880 J=1,N	0360
860	VECT(J,I) = VECT(J,I) - TEMP*VECT(J,K)	0361
	CONTINUE	0362
		363
885	GO TO (890,900) ITER	0364
C	NORMALIZE THE VECTOR	365
900	TEMP = 0.	0366
		0367

```

910      DO 910 J=1,N
          TEMP = TEMP + VECT(J,I)**2
          TEMP = 1.0/SQRTF(TEMP)
          0368
          0369
          0370
          371
          0372
          0373
          374
          0375

      DO 920 J=1,N
          VECT(J,I) = VECT(J,I)*TEMP
          0377
          378
          0379
          380
          381
          382
          0383
          384
          385
          0386
          0387
          0388
          0389
          0390
          391
          0392
          0393
          0394
          0395
          396
          0397
          0398
          0399
          400
          0401
          0402

      C      IF VECTOR ELEMENT IS VERY SMALL, SET IT TO ZERO.
          IF(ABSF(VECT(J,I))-ETA) 919,920,92
          919 VECT(J,I) = 0.0
          920 CONTINUE
          700 CONTINUE

      C      ROTATE CODIAGONAL VECTORS INTO VECTORS OF ORIGINAL ARRAY
      C      - - - - -
      C      LOOP OVER ALL THE TRANSFORMATION VECTORS
          JUMP = NSIZE - (N+1)
          IM = NM1
          DO 950 I=1,NM2
              J1 = JUMP
              C      MOVE A TRANSFORMATION VECTOR OUT INTO BETTER INDEXING POSITION.
              DO 955 J=IM,N
                  B(J,2) = A(J1)
                  J1 = J1 + J
                  955
              C      MODIFY ALL REQUESTED VECTORS.
              DO 960 K=1,NROOT
                  TEMP = 0.
              C      FORM SCALAR PRODUCT OF TRANSFORMATION VECTOR WITH EIGENVECTOR
              DO 970 J=IM,N

```

```

970      TEMP = TEMP + B(J,2)*VECT(J,K)
980      TEMP = TEMP + TEMP
990      DO 980 J=IM,N
1000     VECT(J,K) = VECT(J,K) - TEMP*B(J,2)
1010     CONTINUE
1020     JUMP = JUMP - IM
1030     IM = IM - 1
1040
1050     CONTINUE
1060     RETURN
1070     END
1080
1090     C
1100     SUBROUTINE INPUT(N,NH,NO,IPT,ISTP,AL,TH,PH,BONDL,Z,ZS,BETA,U,COORD
1110     1, AW)
1120     DIMENSION IPT(5), ISTP(18), AL(18), TH(18), PH(18), BONDL(18),
1130     1Z(18), ZS(18), BETA(40), U(40), COORD(3,18), SZ(9), SZS(9),
1140     2SBETA(9), SUS(2,9), SUP(2,9), SAW(9), NOAT(18),
1150     3AW(18), ROX(18,3,3), IST(18), CE(3,18)
1160     C THIS ROUTINE READS IN DATA AND ARRANGES IT SUCH THAT CNDO MAKES USE OF IT.
1170     C N IS THE NUMBER OF ATOMS READ IN. INITIALLY DUMMY ATOMS MAY BE READ IN
1180     C WITH THEIR ATOMIC NUMBER = 0. THEY WILL BE LATER REMOVED IN A
1190     C SUBROUTINE. N IS THUS INITIALLY SET EQUAL TO THE NUMBER OF ATOMS,
1200     C NO IS THE NUMBER OF ORBITALS OCCUPIED.
1210     C IPT IS AN ARRAY OF OPTIONS - SEE CNDO
1220     C ISTP IS THE ARRAY OF STARTING POINTS USED IN CONSTRUCTING CARTESIAN
1230     C COORDINATES FROM BOND ANGLES AND DISTANCES.
1240     C AL IS THE ARRAY OF ANGLES ALPHA
1250     C TH IS THE ARRAY OF ANGLES THETA
1260     C PH IS THE ARRAY OF ANGLES PHI
1270     C BONDL IS THE ARRAY OF BOND LENGTHS
1280     C Z IS THE ARRAY OF CORE CHARGES
1290     C ZS IS THE ARRAY OF SLATER EXPONENTS
1300     C BETA IS THE ARRAY OF BETA ZEROS
1310     C U IS THE ARRAY OF IONIZATION POTENTIALS
1320     C COORD IS THE ARRAY OF CARTESIAN COORDINATES
1330     C AW IS THE ARRAY OF ATOMIC WEIGHTS

```

0403
0404
0405
0406
0407
0408
0409
410
0411
0412
0413


```

C THE FOLLOWING ARRAYS ARE READ IN ONCE AND ARE USED TO CONSTRUCT THE
C ABOVE ARRAYS EACH TIME AN ATOM IS FED IN
C SZ IS ARRAY OF CORE CHARGES
C SZS IS THE ARRAY OF SLATER EXPONENTS
C SBETA IS ARRAY OF BETA ZEROS
C SUS US ARRAY OF IONIZATION POTENTIALS FOR S ORBITALS FOR CNDO/1
C FIRST ROW IS FOR CNDO/1, SECOND ROW FOR CNDO/2
C SUP IS IONIZATION POT. FOR P ORBITALS, FOLLOWING SUS CONVENTION
C SAW IS ARRAY OF ATOMIC WEIGHTS
C SUBROUTINE CONV CONVERTS BOND ANGLES AND DISTANCES INTO CARTESIAN COORD.
C IF(IFBF-12345) 10,20,10
10 READ (50,100) (SZ(I), I = 1,9)
   READ (50,100) (SZS(I), I = 1,9)
   READ (50,100) (SBETA(I), I = 1,9)
   READ (50,100) (SUS(1,I), I = 1,9)
   READ (50,100) (SUP(1,I), I = 1,9)
   READ (50,100) (SUS(2,I), I = 1,9)
   READ (50,100) (SUP(2,I), I = 1,9)
   READ (50,100) (SAW(I), I = 1,9)
   WRITE (51,121)
   WRITE (51,101) (SZ(I), I = 1,9)
   WRITE (51,122)
   WRITE (51,101) (SZS(I), I = 1,9)
   WRITE (51,123)
   WRITE (51,101) (SBETA(I), I = 1,9)
   WRITE (51,124)
   WRITE (51,101) (SUS(1,I), I = 1,9)
   WRITE (51,125)
   WRITE (51,101) (SUP(1,I), I = 1,9)
   WRITE (51,126)
   WRITE (51,101) (SUS(2,I), I = 1,9)
   WRITE (51,127)
   WRITE (51,101) (SUP(2,I), I = 1,9)
   WRITE (51,128)
   WRITE (51,101) (SAW(I), I = 1,9)
   IFBF = 12345

```

```

20 CONTINUE
  READ (50,102)
  WRITE (51,102)
  READ (50,103), N, NH, NO, (IPT(I), I = 1,5)
  IF(N) 1000,1000,21
1000 STOP
21 CONTINUE
  DO 25 I = 1,N
25  READ (50,114) (ISTP(I), NOAT(I), AL(I), TH(I), PH(I), BONDL(I))
    WRITE (51,129)
    DO 26 I = 1,N
26  WRITE (51,130) (ISTP(I), NOAT(I), AL(I), TH(I), PH(I), BONDL(I))
    CALL CONV(N,ISTP,AL,TH,PH,BONDL,NOAT,RCX,IST,CE,COORD)
    NOT = N-NH
    NT = 4*NOT+NH
    DO 30 I = 1,N
    IN = NOAT(I)
    AW(I) = SAW(IN)
    Z(I) = SZ(IN)
30  ZS(I) = SZS(IN)
    IW = IPT(4)
    DO 35 I = 1,NOT
    IM = 4*I-3
    IN = NOAT(I)
    U(IM) = -SUS(IW,IN)
    BETA(IM) = -SBETA(IN)
    IM = IM+1
    IX = IM+2
    DO 35 J = IM,IX
    BETA(J) = -SBETA(IN)
35  W(J) = -SUP(IW,IN)
    NS1 = 4*NOT+1
    DO 40 I = NS1,NT
    W(I) = -SUS(IW,1)
40  BETA(I) = -SBETA(1)
    IF(IPT(1)+1) 45,50,45

```

```

40 WRITE (51,104)
   WRITE (51,105) N,MN,NU, (IPT(I), I = 1,5)
   WRITE (51,106) (Z(I), I = 1,N)
   WRITE (51,107) (Zs(I), I = 1,N)
   WRITE (51,108) (BETA(I), I = 1,NT)
   WRITE (51,109) (U(I), I = 1,NT)
   WRITE (51,110) ((COORD(I,J), I = 1,3), J = 1,N)
   DO 50 I = 1,NT
     BETA(I) = BETA(I)/27.21
     U(I) = U(I)/27.21
   RETURN
100 FORMAT (9F5.3)
101 FORMAT (1H,10F8.3)
102 FORMAT (80H
1
103 FORMAT (812)
104 FORMAT (80H
   NO. ATOMS      NO. H ATOMS      NO. OCCUPIED ORB
   ITALS      BRANCH CODE      )
105 FORMAT (8X,12,17X,12,18X,12,15X,512)
106 FORMAT (16H CHARGES ON CORE)
108 FORMAT (17H SLATER EXPONENTS)
109 FORMAT (11H BETA ZEROS)
110 FORMAT (2H U)
112 FORMAT (12H COORDINATES)
113 FORMAT (1H,5F12.6)
114 FORMAT (12,13,4F10.5)
121 FORMAT (22H TABLE OF CORE CHARGES)
122 FORMAT (26H TABLE OF SLATER EXPONENTS)
123 FORMAT (36H TABLE OF BETA ZEROS, NEGATIVE UNITS)
124 FORMAT (41H TABLE OF IONIZ. POT., S ORBITALS, CNDO/1)
125 FORMAT (41H TABLE OF IONIZ. POT., P ORBITALS, CNDO/1)

```

```

126 FORMAT (39H TABLE OF 0.5*(I+A), S ORBITALS, CNDO/2)
127 FORMAT (39H TABLE OF 0.5*(I+A), P ORBITALS, CNDO/2)
128 FORMAT (23H TABLE OF ATOMIC MASSES)
129 FORMAT (67H STP AT.NO. ALPHA THETA PHI
      1BOND LENGTH )
130 FORMAT (1H ,I3,3X,I3,4F14.6)
      END

      SUBROUTINE CONV(N,ISTP,AL,TH,PH,BONDL,NOAT,ROX,IST,CE,CD)
      THIS SUBROUTINE CONVERTS ARRAYS OF BOND ANGLES AND DISTANCES INTO
      THE ARRAY CD, CARTESIAN COORDINATES.
      DUMMY ATOMS, IDENTIFIED BY NOAT = AT. NO. = ZERO ARE REMOVED FROM THE
      FINAL ARRAY. HYDROGEN ATOMS, IDENTIFIED BY NOAT = 1 ARE PLACED AT
      END OF ARRAY.
      N IS THE NUMBER OF POSITIONS TO BE TRACED OVER
      ISTP IS THE STARTING POINT BEFORE EACH TRACE
      AL, TH, AND PH, CONTAIN THE ANGLES FOR ROTATIONS ABOUT Z, X, THEN Y AXIS
      RESPECTIVELY
      BONDL CONTAINS THE BOND LENGTHS
      AW CONTAINS THE ATOMIC MASSES
      ROX, CE, AND IST ARE WORKING SPACES
      CD IS THE MATRIX OF COORDINATES DETERMINED BY THE PROGRAM
      DIMENSION ISTP(18), AL(18), TH(18), PH(18), BONDL(18), NOAT(18),
      1ROX(18,3,3), IST(18), CD(3,18), CE(3,18)
      DO 217 I = 1,N
      CA = COSF(0.017453293*AL(I))
      SA = SINF(0.017453293*AL(I))
      CT = COSF(0.017453293*TH(I))
      ST = SINF(0.017453293*TH(I))
      CP = COSF(0.017453293*PH(I))
      SP = SINF(0.017453293*PH(I))
      ROX(I,1,1) = CA*CP+SA*ST*SP
      ROX(I,1,2) = -SA*CP+CA*ST*SP
      ROX(I,1,3) = CT*SP
      ROX(I,2,1) = SA*CT
      ROX(I,2,2) = CA*CT

```

```

      ROX(I,2,3) = -ST
      ROX(I,3,1) = -CA*SP+SA*ST*CP
      ROX(I,3,2) = SA*SP+CA*ST*CP
217  ROX(I,3,3) = CT*CP
      IA = 0
      IB = 0
230  IF(IA-N) 235,4,4
235  IA = IA+1
      IAL = IA-1
      IF(IAL) 280,280,240
240  IF(ISTP(IA)-IB) 245,245,270
C
C   BEGIN RETRACE TO PREVIOUS STARTING POINT
C
245  ISTX = IST(IB)
      DO 260 I = 1,IAL
260  CD(1,I) = CD(1,I)+BONDL(ISTX)
      DO 262 I = 1,3
      DO 262 J = 1,IAL
      CE(I,J) = 0.0
      DO 262 K = 1,3
262  CE(I,J) = CE(I,J)+ROX(ISTX,K,I)*CD(K,J)
      DO 263 I = 1,3
      DO 263 J = 1,IAL
263  CD(I,J) = CE(I,J)
      IB = IB-1
      IF(ISTP(IA)-IB) 245,245,270
C
C   ADDITION IF IA-TH ATOM
C
270  DO 272 I = 1,3
      DO 272 J = 1,IAL
      CE(I,J) = 0.0
      DO 272 K = 1,3
272  CE(I,J) = CE(I,J)+ROX(IA,I,K)*CD(K,J)
      DO 273 I = 1,3

```



```

DO 273 J = 1,IA1
273 CD(I,J) = CE(I,J)
DO 275 I = 1,IA1
275 CD(1,I) = CD(1,I)-BONDL(IA)
280 DO 285 I = 1,3
285 CD(I,IA) = 0.0
IB = IB+1
IST(16) = IA
GO TO 230

```

```

C
C REARRANGE ATOMS
C

```

```

4 NO = N
DO 30 I = 1,N
IF(NOAT(I)) 30,10,30
10 DO 20 J = 1,N
J1 = J+1
NOAT(J) = NOAT(J1)
DO 20 K = 1,3
20 CD(K,J) = CD(K,J1)
NOAT(N) = 1
NO = NO-1
I=I 1
30 CONTINUE
N = NO

```

```

C
C ARRANGE HYDROGEN ATOMS LAST
C

```

```

DO 50 I = 1,N
IF(NOAT(I)-2) 40,40,50
40 I1 = I+1
DO 42 J = 11,N
IF(NOAT(J)-2) 42,42,43
42 CONTINUE
GO TO 60
43 DO 44 K = 1,3

```

```

44 CE(K,1) = CD(K,J)
   ISN = NOAT(J)
   JS = J+1
   NO = J-I
   DO 45 K = 1,NO
     JS = JS-1
     JS1 = JS-1
     NOAT(JS) = NOAT(JS1)
     DO 45 L = 1,3
       45 CD(L,JS) = CD(L,JS1)
       DO 46 L = 1,3
         46 CD(L,I) = CE(L,1)
         NOAT(I) = ISN
50 CONTINUE
60 RETURN
END
END

```

FINIS

-EXECUTE.

1	1	2	3	4	5	6	7
12	65	975	15	1625	195	2275	26
9	13	17	21	25	31	39	
1306	539	932	1405	1944	2558	3238	4020
	354	596	830	1067	1319	1585	1866
7176	3106	5946	9594	14051	19316	25390	32272
	1258	2563	4001	5572	7275	9111	11010
1	7	9	11	12	14	16	19
1	ETHANE	STAGGER					
10	6	7	0	215			
1	6						
2	1		120.0	110.86		1.102	
2	1			110.86		1.102	
2	1		120.0	110.86		1.102	
2	6		60.0			1.4660	
3	1		60.0	-69.14		1.102	
3	1		180.0	-69.14		1.102	

3	1	60.0	-69.14	1.102
2				.775
3			-90.	
1	ETHANE (ECLIPSED)			
10	6 7 1	250		
1	6			
2	1	120.0	111.28	1.102
2	1	120.0	111.28	1.102
2	1		111.28	1.102
2	6			1.4633
3	1	60.00	-68.72	1.102
3	1	180.0	-68.72	1.102
3	1	60.00	-68.72	1.102
2				.775
3			-90.	

APPENDIX

II Computer output of Water (H₂O) (Sample calculation)

H2O OPTIMIZE						
STP	AT. NO.	ALPHA	THETA	PHI	BOND LENGTH	
1	8	-0	-0	-0	-0	
2	1	52.110000	-0	-0	1.028900	
2	1	-52.110000	-0	-0	1.028900	
2	-0	-0	-0	-0	-0	
NO. ATOMS NO. F ATOMS NO. OCCUPIED ORBITALS BRANCH CODE						
3 2 4 1 0 0 250						
CHARGES ON CORE						
6.000 1.000 1.000						
SLATER EXPONENTS						
2.275 1.200 1.200						
BETA ZEROS						
-31.000 -31.000 -31.000 -31.000 -9.000 -9.000						
U -25.390 -9.111 -9.111 -9.111 -7.176 -7.176						
COORDINATES						
.63189631 -.81199893 0 0						
.63189631 .81199893 0 0						
COORDINATES IN ATOMIC UNITS						
1.194134 -1.534485 0 0						
1.194134 1.534485 0 0						
DIRECTION COSINES						
0 .614147 .614147						
-.614147 0 .000000						
-.614147 -.000000 0 0						
0 -.789191 .789191						
.789191 0 1.000000						
-.789191 -1.000000 0 0						
0 0 0 0 0 0						
0 0 0 0 0 0						
DISTANCES IN ATOMIC UNITS						
0 1.944377 1.944377						
1.944377 0 3.068970						
1.944377 3.068970 0						

RHO									
	0								
	3.378355	3.378355	3.378355						
	3.378355	0	3.682764						
	3.378355	3.682764	0						
TAU									
	0								
	-.309353	.309353	.309353						
	-.309353	0	0						
	-.309353	0	0						
OVERLAP									
	1.000000	0	0						
	0	1.000000	0						
	0	0	1.000000						
	0	0	0						
	.434263	.220063	-.282785						
	.434263	.220063	.282785						
GAMMA									
	.826465	.476151	.476151						
	.476151	.750000	.320779						
	.476151	.320779	.750000						
V									
	0	.476151	.476151						
	2.856904	0	.320779						
	2.856904	.320779	0						
F									
	-.933113	0	0						
	0	-.334840	0						
	0	0	-.334840						
	0	0	0						
	-.319194	-.161751	.207853						
	-.319194	-.161751	-.207853						

ORBITAL ENERGIES						
-1.442662	-.759905	-.701810	-.654866	.289195	.309628	
C						
.880226	.051057	-0	.000000	.333614	.333614	
.000000	-.000000	.753527	.000000	-.464864	.464864	
-.295445	.836979	.000000	-.000000	.325713	.325713	
.000000	-.000000	.000000	-1.000000	-.000000	-.000000	
-.371370	-.544848	-.000000	.000000	.531613	.531613	
.000000	.000000	-.657417	.000000	-.532824	.532824	
P						
1.724169	-.404680	.000000	.000000	.394850	.394850	
-.404680	1.406282	.000000	-0	.579297	.579297	
.000000	.000000	1.135605	-.000000	-.700575	.700575	
.000000	-0	-.000000	2.000000	.000000	-0	
.394850	.579297	-.700575	.000000	.866972	.002577	
.394850	.579297	.700575	-0	.002577	.866972	
PA						
6.266056	.866972	.866972				
F						
-1.139160	.167227	-0	-0	-.413198	-.413198	
.167227	-.409526	-0	0	-.299668	-.299668	
-0	-0	-.297673	.000000	.374643	-.374643	
-0	0	.000000	-.654869	-.000000	0	
-.413198	-.299668	.374643	-.000000	-.229602	-.076986	
-.413198	-.299668	-.374643	0	-.076986	-.229602	
ENERGY						
-17.570850	-.752501	-.752501				
-.412826	.010344					
-.412826						
10 ITERATIONS						
-19.80115807						

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<p>The approximate Self-Consistent Field Molecular Orbital Theory (ASCFM) with complete neglect of differential overlap (CNDO) has been applied to the calculation of electronic structure for several selected molecules in this text. The theory leads to calculated equilibrium geometry configurations and the barrier to internal rotation of ethane, inversion barrier of ammonia and the barrier for cis to trans conversion for difluorodiazine. These results are in reasonable agreement with experimental values in most cases. The stretching force constants are higher than experimental values by a factor of approximately two. The orbital energy levels for ammonia and for oxygen difluoride as a function of bond angles were in reasonable agreement with the full LCAO-SCF Calculations. A variation of parameters to find a new set of parameters was attempted with unsuccessful results.</p> <p>The extended Hückel Theory (EH) can be applied to aliphatic hydrocarbons but its application to non-hydrocarbon molecules is quite limited.</p>			

14.	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
	Approximate Self-Consistent field theory Extended Huckel Molecular Orbital Theory Complete Neglect of Differential Overlap Barrier -- NH_3 (inversion) C_2H_6 (eclipsed to stagger form) N_2F_2 (cis to trans) LCAO-SCF (Linear Combination of Atomic Orbital Self-Consistent Field) force constant equilibrium geometry (Bond length and Bond angle) ground singlet and doublet states Energy level diagram for F_2O NH_3 J.A. Pople R. Hoffmann						





121

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